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Procedures for Applying City-Specific EKMA

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16. ABSTRACT

OZIPM-4 is a model which allows the user to estimate the volatile organic compound (VOC) control requirement for a city in order to achieve the national ambient air quality standard for ozone.

This manual outlines the inputs required to run OZIPM-4 and explains how to develop the needed variables.

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July 1989

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PREFACE

This document is one of five related to application of EKMA and the use of OZIPM-4 (Ozone Isopleth Plotting with Optional Mechanisms), the computer program used by EKMA. Listed below are the titles of the five documents and a brief description of each.

"Procedures for Applying City-specific EKMA", EPA-450/4-89-012, July 1989

- Describes the procedures for using the Empirical Kinetic Modeling Approach (EKMA). The major focus is on how to develop needed inputs for OZIPM-4. In addition this document describes how to determine a control target once OZIPM-4 has been run.

"A PC Based System for Generating EKMA Input Files", EPA-450/4-88-016, November 1988

- Describes a program that creates EKMA input files using a menu driven program. This sofware is only available for an IBM-PC or compatible machine. Files built using this system can be uploaded to a mainframe computer.

"User's Manual for OZIPM-4 (Ozone Isopleth Plotting with Optional Mechanisms)-Volume 1", EPA-450/4-89-009a, July 1989

- Describes the conceptual basis behind OZIPM-4. It describes the chemical mechanism, Carbon Bond 4, and each of the options available in OZIPM-4. Formats for each of the options are outlined so that a user can create input files using any text editor.

"User's Manual for OZIPM-4 (Ozone Isopleth Plotting with Optional Mechanisms)-Volume 2: Computer Code", EPA-450/4-89-009b, July 1989

- Describes modifications to the computer code that are necessary in order to use OZIPM-4 on various machines. A complete listing of OZIPM-4 is also found in this publication.

"Consideration of Transported Ozone and Precursors and Their Use in EKMA", EPA-450/4-89-010, July 1989

- Recommends procedures for considering transported ozone and precursors in the design of State Implementation Plans to meet national ambient air quality standards for ozone. A computerized (PC) system for determining whether an ozone exceedance is due to overwhelming transport is described. This document is necessary, only if an area is suspected of experiencing overwhelming transport of ozone or ozone precursors.

EKMA may be used in several ways: (1) as a means for helping to focus more resource-intensive photochemical grid modeling analyses on strategies most likely to be successful in demonstrating attainment; (2) as a procedure to assist in making comparisons between VOC and NOx controls; (3) in non-SIP applications, such as in helping to make national policy evaluations assessing cost/benefits associated with various alternatives and (4) for preparation of control estimates consistent with limitations/provisions identified in Clean Air Act Amendments.

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1.0 INTRODUCTION

In March of 1981, the U.S. Environmental Protection Agency (EPA) issued guidelines for applying the city-specific Empirical Kinetics Modeling Approach (EKMA) (Gipson, et al, 1981). EKMA is a procedure that can be used to estimate emission reductions that are needed to achieve the national ambient air quality standard (NAAQS) for ozone. Application of city-specific EKMA according to the March 1981 guidelines entails using the Ozone Isopleth Plotting Package (OZIPP) to relate peak ozone concentrations to its precursors--nonmethane organic compounds (NMOC) and oxides of nitrogen (NO_x) (Whitten and Hogo, 1978; and EPA, 1978). OZIPP is a computer program that incorporates a simplified trajectory model and a chemical kinetics mechanism (known as the DODGE mechanism) that mathematically simulate ozone formation. After the issuance of the March 1981 guidelines, the use of other chemical mechanisms with EKMA was suggested (Jeffries, et al, 1981; and Carter, et al, 1982). In response, supplemental guidance on using other mechanisms was circulated to EPA Regional Offices in December of 1981 (Rhoads, 1981). Specific guidance regarding the use of one alternative mechanism-the Carbon Bond III mechanism (CB-3)--was issued in February of 1984 (Gipson, 1984).

Since 1984, newer chemical mechanisms have been developed (Gery, et al, 1988; and Lurmann, et al, 1987). This document focuses on information necessary to apply EKMA utilizing the Carbon Bond IV mechanism (CB-4) and provides details on all necessary input parameters. The discussions that follow will focus exclusively on using the CB-4 mechanism with the OZIPM4 program. This program, Ozone Isopleth Plotting With Optional Mechanisms 4 (OZIPM4), is an updated version of OZIPP which contains the most recent chemical kinetics and stoichiometric information. Any application of EKMA should be carried out with the OZIPM4 code described in EPA (1989).

The remainder of this document is divided into two chapters. Chapter 2 contains a discussion of the CB-4 mechanism and its relationship to the OZIPM4 program. Chapter 3 describes the information necessary to develop input data suitable for use of EKMA/CB-4.

In the OZIPM4 model, a column of air containing ozone and precursors is transported along an assumed straightline trajectory. The trajectory is defined so that the simulated column of air over the city being simulated arrives at the site observing the daily maximum ozone concentration at the time of the observed maximum. As the column moves, it encounters gridded emissions of fresh precursors that are mixed uniformly within the column. The column is assumed to extend from the earth's surface through the mixed layer. The assumed horizontal dimensions of this column are such that the concentration gradients are small enough to make the horizontal exchange of air between the column and its surroundings insignificant. The air within the column is assumed to be uniformly mixed at all times.

At the beginning of a simulation, the column is assumed to contain some specified initial concentrations of NMOC, NO_x, and CO. As the column moves along the assumed trajectory, the height of the column will change because of variations in mixing height; it is assumed to change with time during a user-selected period (for example, 8 a.m. - 3 p.m.), and to be constant before and after that period. As the height of the column increases, its volume increases, and air above from the inversion layer is mixed in. Pollutants above the mixed layer are described as "transported above the surface layer" or "transported aloft." Any ozone or ozone precursors above the mixed layer that are mixed into the column as it expands are assumed to be rapidly mixed throughout the column.

Concentrations of NMOC species, NO, NO_2, CO, and O_3, within the column are physically decreased by dilution due to the inversion rise, and physically increased both by entrainment of pollutants transported aloft and by fresh emissions. All species react chemically according to the kinetic mechanism selected. Photolysis rates within that mechanism are functions of the intensity and spectral distribution of sunlight, and they vary diurnally according to time of year and location.

2.0 THE CB-4 MECHANISM

As the name implies, CB-4 is the fourth in a series of evolving chemical kinetics mechanisms. Each of the successive carbon bond mechanisms contains revisions that reflect increased knowledge of the photochemistry leading to ozone formation. The CB-4 mechanism is currently the most recent version of that generic series. It has been designed to simulate laboratory smog chamber experiments using detailed data bases, as well as atmospheric situations in which much less information is typically available. While a comprehensive discussion of the scientific basis of the CB-4 mechanism is beyond the scope of this document, some introductory material on basic concepts is included below for those unfamiliar with CB-4.

A distinguishing feature of any chemical mechanism is the manner in which organic reactivity is treated. Because the construction and use of a mechanism that includes all atmospheric species is virtually impossible, individual organic species must be combined, or lumped, into some sort of functional group or groups. Thus, the discussion of any chemical mechanism must necessarily address the manner in which organic chemistry is represented in the mechanism. The concepts underlying the treatment of organic reactivity in CB-4 are discussed in Section 2.1 below.

As noted in Section 1.0, use of the CB-4 mechanism in a city-specific EKMA analysis is most easily accomplished with the OZIPM4 computer program.

2.1 Organic Reactivity

As described in Section 2.0, a characteristic that typically distinguishes chemical mechanisms is the manner in which organic compounds are represented in the mechanism. A number of approaches have been taken, but most have focused on lumping similar species into a single, identifiable molecular species that represents the chemistry of that particular class of compounds. For example, propylene might be used to represent the chemistry of all alkenes. The CB-4 mechanism is somewhat different in that the primary functional organic groups are based on various types of structural units (e.g., single-bonded carbon atoms) as opposed to molecular type (e.g., alkanes). As will be seen below, this kind of structuring results in some organic species being partitioned among more than one functional group.

In CB-4, nine functional groups are used to represent organic species, each based on various types of carbon bonds:

(1) single-bonded paraffinic carbon atoms, and represented by PAR;

(2) slowly reacting olefinic double bonds, almost exclusively ethylene and represented by ETH;

(3) relatively reactive olefinic double bonds, and represented by OLE;

(4) less reactive aromatic compounds represented by TOL;

(5) more reactive aromatic compounds represented by XYL;

(6) formaldehyde represented by FORM;

(7) acetaldehyde and high aldehydes represented by ALD2;

(8) isoprene, represented by ISOP;

(9) nonreactive compounds represented by NR.

Just as important as the definition of the functional groups themselves is the manner in which individual organic species are apportioned to those groups. As noted above, a particular organic compound is assigned to a CB-4 group, or groups, on the basis of molecular structure. To illustrate the procedure, consider the propene molecule which contains one single carbon-bond and one double carbon-carbon bond (see Figure 2-1). In the CB-4 mechanism, the propene molecule is represented by one paraffin and by one olefin. In essence, the molecule has been apportioned on the basis of the carbon-carbon bonds: the double bond represented by OLE, and the one single bond by PAR. Similar classifications have been determined for hundreds of other compounds, and they provide the basis for establishing the overall reactivity of an urban mix.

In the propene example illustrated in Figure 2-1, note that the number of carbon atoms associated with PAR is one, while the number for OLE is two. A general principle underlying use of the carbon bond mechanism is that the number of carbon atoms associated with any individual carbon bond group is fixed. (Table 2-1 shows these characteristic carbon numbers for the carbon bond functional groups.) By making use of the carbon numbers, concentrations of each CB-4 group can be determined from concentrations of individual organic species. To illustrate, consider the propene example discussed above, and further assume that the concentration of propene is 3 ppmC. Since propene is represented in CB-4 by one PAR and by one OLE, the 3 ppmC total propene concentration must be apportioned to these two carbon bond groups. Of the three carbon atoms in a propene molecule, one is PAR and two are OLE (see Figure 2-1). Thus, one-third of the carbon atoms can be thought of as PAR, and two-thirds as OLE. Since concentration is proportional to the number of carbon atoms, the concentrations of PAR and OLE in the CB-4 mechanism would be 1 ppmC and 2 ppmC, respectively.* This same concept can be extended to multicomponent mixtures as well. In such cases, concentrations of the

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*i.e., $C_{PAR} = 1/3 \times 3$ ppmC and $C_{OLE} = 2/3 \times 3$ ppmC

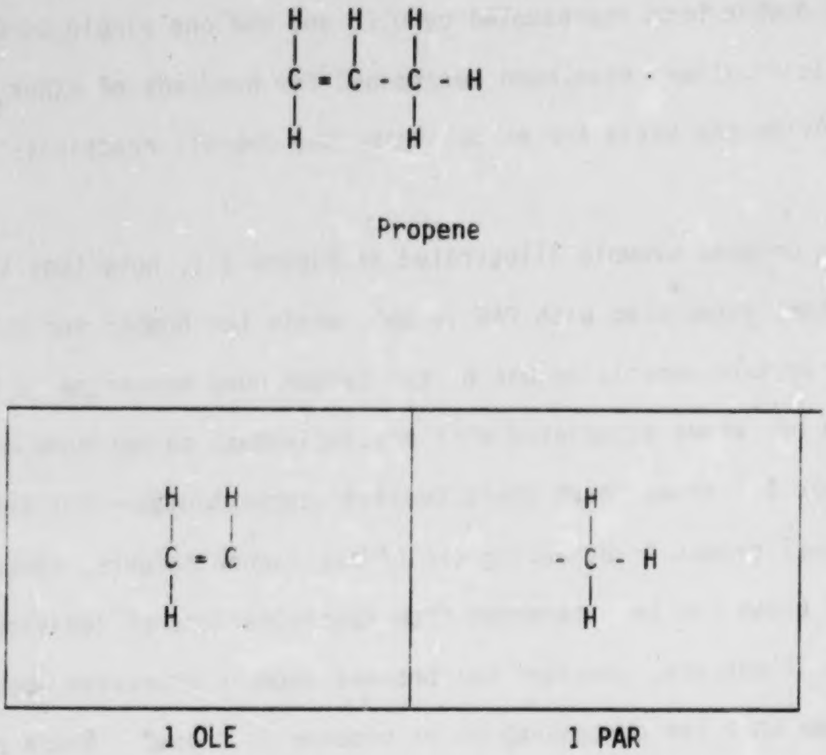
Propene
1 OLE
1 PAR

Figure 2-1. Example of Carbon Bond Lumping Procedure

TABLE 2-1

CARBON NUMBERS FOR CB-4 ORGANIC SPECIES

Carbon Bond Group	Carbon Number (carbon atoms per molecule)
PAR	1
ETH	2
OLE	2
TOL	7
XYL	8
FORM	1
ALD2	2
NR	1
ISOP	5

individual organic species are first apportioned to their respective CB-4 group. The total concentration of any particular CB-4 group is then obtained by summing the contributions due to the individual organic species. This procedure will be more fully discussed in Appendix C.

In using the CB-4 mechanism with the OZIPM4 program, absolute concentrations of the individual CB-4 groups are not directly input to the model. Rather, the total NMOC concentration is specified, and the fraction of carbon attributable to each CB-4 group is input. For example, assume that the total NMOC concentration is 2.0 ppmC, of which 1.4 ppmC is PAR (as determined by the procedure described in the preceding paragraph). Then the apportioning factor, or carbon fraction, for PAR would be 0.70, indicating that 70 percent of the total carbon is categorized as PAR. A special set of default values for CB-4 fractions is normally used. These defaults were derived from 1984-86 NMOC species data collected in many cities (Jeffries, 1987).

2.2 Use of CB-4 in OZIPM4

The CB-4 mechanism that is contained in OZIPM4 is outlined in Appendix A. A discussion of the development and testing of this mechanism is contained in Gery, et al, 1988. More extensive information on the evolution of the carbon bond mechanism in general can be found in Killus and Whitten, 1983; Killus and Whitten, 1982; Whitten and Hogo, 1977; Whitten, et al, 1980; Whitten, et al, 1979.

The specific inputs necessary to use CB-4 in OZIPM4 are contained in EPA, 1988 and EPA 1989. The discussions in Section 2.1 and above have provided a general overview of the CB-4 mechanism and its relationship to the OZIPM4 program. In most instances, consideration of the details of the mechanism will not be required in any particular model application. The major concern in most applications is the determination of the total NMOC concentration. In cases where defaults are not used, specification of the carbon bond fractions required to apportion the total carbon concentration to the individual carbon bond groups (i.e., PAR, ETH, OLE, TOL, XYL, FORM, ALD2, ISOP, and NR) is also of concern. The procedures for developing these and other model inputs for an EKMA application are the subject of the next chapter.

3.0 PROCEDURES FOR APPLYING EKMA/CB-4

Although the March 1981 guidelines deal explicitly with OZIPP and the DODGE mechanism, many of the concepts described in that document are relevant to the use of EKMA with OZIPM4 and the CB-4 mechanism. For example, selecting the cases to model is unaffected by choice of chemical mechanism. Nevertheless, use of CB-4 with OZIPM4 does require some special considerations. This chapter will focus primarily upon these circumstances, but will also describe all other facets of conducting an EKMA modeling analysis.

The ensuing discussion of using CB-4 with EKMA can perhaps be facilitated by a brief overview of the general modeling procedure. While the following section describes EKMA in terms of ozone isopleth diagrams, it is no longer necessary to develop these diagrams in order to determine the VOC control requirements. By using the EKMA option the control requirement is determined without drawing isopleth diagrams. The OZIPM4 program is used to generate ozone isopleth diagrams that explicitly relate peak hourly ozone concentrations to initial (i.e., 8 a.m.) ambient levels of the ozone precursors NMOC and NO_x (see Figure 3-1). The diagrams are used with a measured peak ozone concentration and a city's NMOC/NO_x ratio to compute, on a percent basis, the VOC emission reduction needed to lower the observed peak to the level of the standard. While isopleth diagrams are explicit functions of initial NMOC and NO_x, the positioning of the ozone isopleths on the diagram is affected by model input variables that are related to meteorology, emissions occurring throughout the day, and pollutants transported from areas upwind of the city under review. Because these factors vary from day to day, the

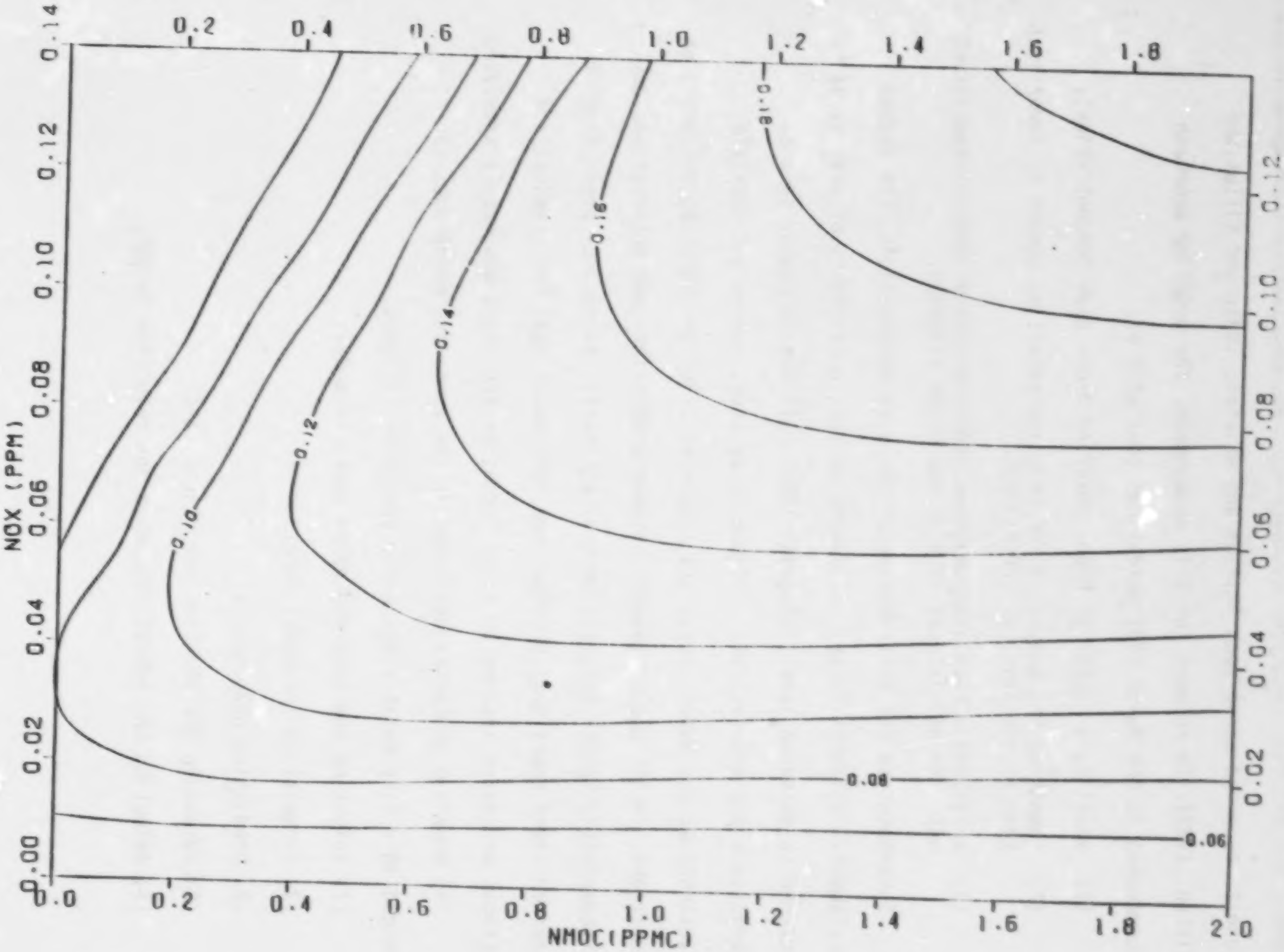

FIGURE 3-1. OZIPM4 EXAMPLE ISOPLETH RUN

highest VOC emission reduction estimate will not necessarily correspond to the highest, observed ozone peak (Killus and Whitten, 1983; and Killus and Whitten, 1982). To account for this phenomenon, the modeling approach recommended in the March 1981 guidelines consisted of:

(1) modeling a number of high, observed ozone peak concentrations;

(2) computing the amount of VOC emission reduction needed to lower each peak to the level of the standard;

(3) selecting a final VOC emission reduction target that is consistent with the statistical form of the ozone standard.

Subsequent to the distribution of these recommendations, EPA issued supplemental guidance further recommending that predictions of peak ozone be compared to observed levels (Rhoads, 1981). If the agreement between predictions and observations is found to be poor, review and possible adjustment to key model inputs are suggested prior to computing VOC emission reductions. While good agreement between predictions and observations does not completely ensure accurate control estimates, successful prediction of observed ozone peaks does provide some confidence that the chemical and physical processes leading to ozone formation are being adequately simulated.

The modeling procedure described in the preceding paragraphs can be divided into five basic steps which should be followed:

(1) selecting the observed ozone peaks to model;

(2) formulating the model inputs;

(3) predicting peak ozone;

(4) computing VOC emission reductions; and

(5) selecting the overall VOC emission reduction target.

3.1 Selection of Modeling Cases

As noted in Section 3.0, the highest VOC control estimate may not correspond to the highest observed ozone concentration. Further, the statistical form of the ozone NAAQS permits on average, one daily maximum 1-hour average ozone concentration above 0.12 ppm per calendar year at each site. Consideration of these two factors led to the recommendation that a number of observed peaks above 0.12 ppm be modeled for each site. The VOC emission reduction target is then selected from these results in a manner that is consistent with the statistical form of the ozone NAAQS. For an EKMA/CB-4 analysis, the same procedure is recommended.

Recommended Procedure: The five (5) highest daily, maximum ozone concentrations at each site should be selected as candidates for modeling. Only ozone peaks that occur within or downwind of the urban area under review should be included. The five highest such values should generally be chosen from the most recent 3 years during which measurements were made at a site.

A State may choose to include an additional year if data from another ozone season become available between the time of the SIP call and the time when the analysis is conducted. While an additional year may be added, a year may not be replaced (i.e., 4 years of data must be used). If 4 years of data are included, the six (6) highest daily, maximum ozone concentrations at each site should be selected as candidates for modeling. If there is a tie for the last daily maximum value, both days should be modeled. In the event that a significant amount of time (a few years) passes between the time of the SIP call and the start of the modeling analysis, the appropriate EPA Regional office should be contacted to determine the appropriate years to model.

In some cases, it may happen that on days initially selected as candidates for modeling, daily maximum ozone (O_3) is most likely the result of "overwhelming transport" from upwind areas. That is, it is unlikely that locally generated emissions have an appreciable effect on the observed daily maximum. Procedures for determining whether an observed daily maximum results from overwhelming transport are described in detail by Meyer and Baugues (1989). In general, overwhelming transport is a strong possibility if the daily maximum occurs before 10 a.m. or if the timing of the observed maximum is inconsistent with available 10 a.m. - 4 p.m. surface wind data and the orientation of the monitoring site with respect to the Metropolitan Statistical Area (MSA) under review. Even if it is likely that an observed daily maximum O_3 concentration results from overwhelming transport, it is possible that the selected day should still be modeled. This would be appropriate if the following occurred: (a) concentrations greater than 0.12 ppm occurred at other times of the day; (b) surface wind data and monitor orientation were consistent with impacts from the local MSA at these times; and (c) the O_3 concentration judged to result from local emissions was one of the top five local peaks. Unless all of the preceding three conditions are met, the day should be discarded and replaced by the previously unselected day having the highest observed daily maximum. Overwhelming transport can also affect selection of which estimate for VOC and/or NO_x controls is needed to attain the NAAQS. This latter issue is addressed in Section 3.5.

3.2 Development of Model Inputs

As just described, the five or six highest, daily maximum ozone peaks at each site are selected for modeling. Two basic objectives of the modeling analysis are to predict the observed ozone peaks, and to compute the VOC emission reductions needed to lower each observed peak to the level of the ozone NAAQS. To best accomplish these objectives, the model inputs should be based on the atmospheric conditions associated with each observed peak. Thus, their derivation ought to be done on a case-by-case basis. In some instances, however, insufficient or inadequate data preclude such a determination, and appropriate approximations or defaults are needed. The major purpose of this section is to describe the methodologies recommended for deriving the model input values under both sets of circumstances.

Table 3-1 summarizes the model input variables that require consideration, regardless of the intended purpose of the model simulation. Before discussing each of the model input variables, one additional point should be added. The recommendations discussed below deal with model inputs that correspond to conditions associated with the observed ozone peak (i.e., so called base-case conditions). Some of these conditions might be expected to change in future years subsequent to the implementation of VOC control programs. Factoring these potential changes into the modeling analysis will be discussed in Section 3.4. Thus, the recommendations discussed below concerning the derivation of model input values will necessarily focus on data corresponding to emissions and atmospheric conditions associated with a particular ozone peak observed in the base case.

3.2.1 Light Intensity

The OZIPM4 program uses a city's latitude, longitude, and time zone, and the day of the year being modeled to generate the appropriate diurnal pattern of photolytic reaction rates. While updates have been made to some of the photolytic rates, these have been incorporated in the OZIPM4 computer code. Thus, no changes need be made for this set of model inputs.

The correct set of numerical time zones for the continental United States is as follows:

Numerical Time Zone	Common Name
4.0	Eastern Daylight Time
5.0	Central Daylight Time
6.0	Mountain Daylight Time
7.0	Pacific Daylight Time

Table 3-1

OZIPM4/CB-4 MODEL INPUTS

Model Input Variables	Section Addressed
Sunlight Intensity	3.2.1
Dilution	3.2.2
Post-0800 Emissions	3.2.3
Ozone Transport	3.2.5
Precursor Transport	3.2.6
Reactivity	3.2.4, 3.2.7
Temperature	3.2.8
Water Vapor	3.2.9
Biogenic Emissions	3.2.10

To produce standard time simulations, even though the output will show daylight time units, a false time zone of one unit (hour) more can be used. Thus, Pacific Standard Time photolysis constants would be generated if a 8.0 were entered instead of the correct 7.0 time zone.

Recommended Procedure: To properly simulate light intensity in OZIPM4, input the city's latitude, longitude, time zone, and the day of the year being modeled.

3.2.2 Dilution

In the OZIPM4 model, dilution occurs as a result of the rise in atmospheric mixing height that typically occurs between early morning and mid-afternoon. The mixing height can be viewed as the top of a surface based layer of air which is well-mixed due to mechanical and thermal turbulence. Specific inputs to OZIPM4 include the early morning mixing height, the maximum afternoon mixing height, the time that the mixing height rise begins, and the time at which the maximum mixing height is finally attained. Procedures for estimating the early morning mixing height and maximum afternoon mixing height from available radiosonde measurements are outlined in Appendix B of this document. The OZIPM4 program will internally calculate the rate of rise in mixing height based upon a characteristic curve developed by Schere and Demerjian (EPA 1981; Schere, et al, 1977).

Recommended Procedure: It is recommended that city-specific estimates of 0800 LCT mixing height and maximum afternoon mixing height be computed using procedures outlined in Appendix B. Minimum 0800 LCT mixing height used should be 250 meters.

3.2.3 Post-0800 Emissions

Post-0800 emissions refer to emissions occurring along the trajectory subsequent to the start of the model simulation. The actual model inputs are expressed as emission densities (kg/km^2) of NMOC, NO_x, and carbon monoxide (CO) concentrations that should be added each hour to represent the effect of fresh precursor emissions. The requirements have changed from the March 1981 guidelines in two respects: (a) large point sources of NO_x are differentiated from other sources and (b) CO emissions are considered.

The following example illustrates how to determine which county's emissions should be used for each hour. Figure 3-2 shows an example trajectory. In this case the peak ozone occurs in Rockdale County between 3 and 4 p.m. The parcel starts at 8 a.m. in Fulton County. Between 8 a.m. and 4 p.m. are 8 hours, indicated on the straight-line trajectory in Figure 3-2. Each value on this line represents the location of the parcel at 1 through 8 hours.

During hour 1 (8-9 a.m.), the parcel is entirely in Fulton County. Emissions for 8-9 a.m. from Fulton County should be used in OZIPM4. During the second hour the parcel moves into Dekalb County. Emissions for 9-10 (hour 2) should be averaged between Fulton and Dekalb Counties. During hours 3 through 6, the parcel is entirely in Dekalb County and emissions should be based upon Dekalb County. During hour 7, the parcel crosses into Rockdale County. Emissions for hour 7 (2-3 p.m.) should be averaged between Dekalb and Rockdale counties. Emissions for hour 8 should be from Rockdale County.

In developing post-8 a.m. emission densities for EKMA, it is necessary to determine whether significant NO_x point sources have effective stack heights greater than the initial mixing height (usually 250 meters). If the effective stack height is greater than the initial mixing height, the NO_x emissions from that source will not be contained within the mixed surface

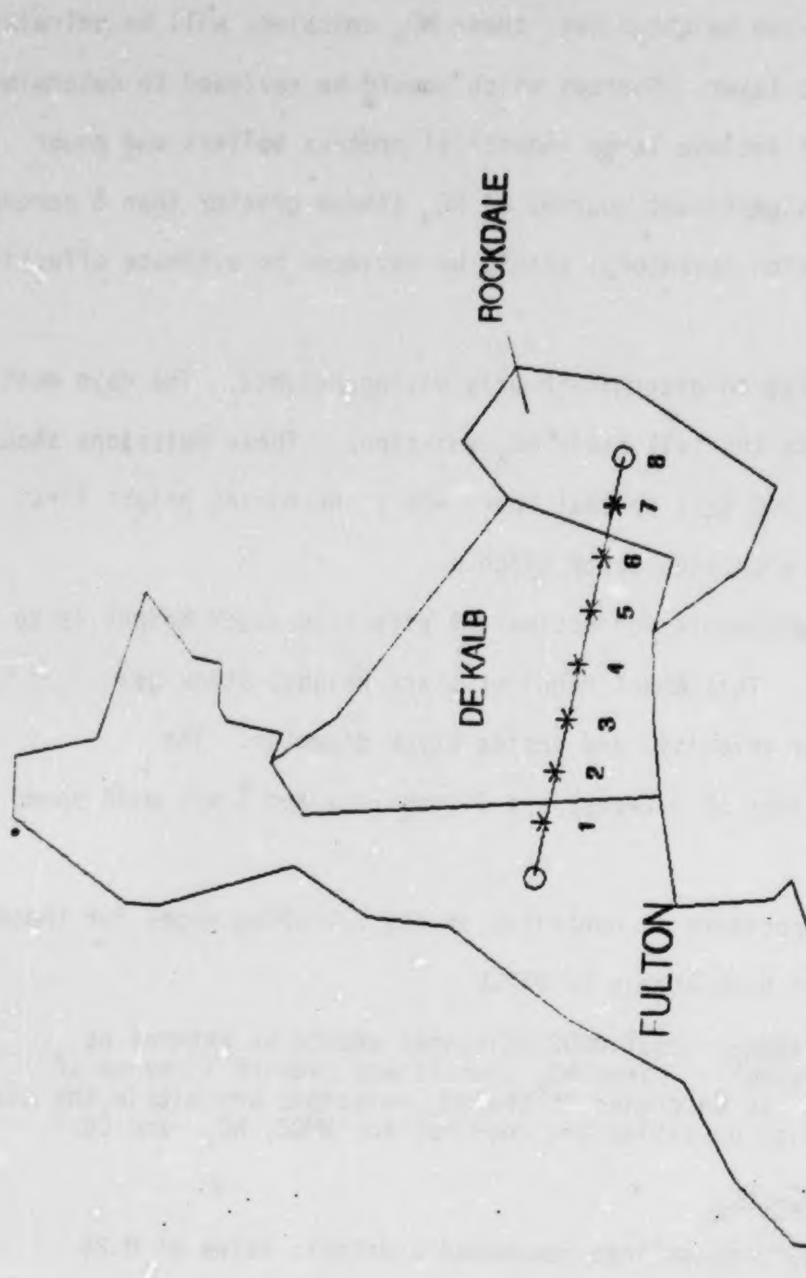
ROCKDALE
DE KALB
FULTON
1
2
3
4
5
6
7
8

FIGURE 3-2 EXAMPLE DETERMINATION OF HOURLY EMISSIONS

layer during the first few hours of the OZIPM4 simulation. At sometime later in the day, as the mixing height rises, these NO_x emissions will be entrained into the mixed surface layer. Sources which should be reviewed to determine effective stack height include large industrial process boilers and power plant boilers. Only significant sources of NO_x (those greater than 5 percent of the total NO_x emission inventory) should be reviewed to estimate effective stack height.

Each day is modeled to determine hourly mixing heights. The days must then be rerun adding in the tall stack NO_x emissions. These emissions should be added to the hour (and _only_ to that hour) where the mixing height first equals or exceeds the effective stack height.

The recommended procedure for estimating effective stack height is to run PTPLU (EPA, 1982). This model requires stack height, stack gas temperature, stack gas velocity, and inside stack diameter. The meteorological conditions of interest are C stability and 5 m/s wind speed (at 10 meter height).

An alternative procedure is contained on the following pages for those individuals who do not have access to PTPLU.

Recommended Procedure: Post-0800 emissions should be entered as emission densities (kg/km^2). Large NO_x sources may require a review of effective stack height to determine if the NO_x emissions are within the mixed surface layer. Emission densities are required for NMOC, NO_x, and CO.

3.2.4 _Initial NO_2/NO_x_

The March 1981 guidelines recommend a default value of 0.25. Review of recent data indicates that this ratio may vary over a wide range (.1-.9) and that "median" ratios for individual cities may also vary significantly. Modeling analyses have indicated that EKMA-CB4 is not sensitive to this ratio. Thus the default value of 0.25 should be used.

Recommended Procedure: A city-specific value for the nitrogen dioxide to oxides of nitrogen ratio $[(NO_2)/NO_x]$ need not be estimated. The default value of 0.25 should be used.

3.2.5 Ozone Transport

The two possible mechanisms by which ozone is transported into an urban area are:

1. Advection of ozone along the earth's surface, and

2. Advection of ozone aloft, typically at night and during early morning hours above the ground-based mixed layer, with downward mixing when the mixing layer increases later in the day.

Ozone transported at the surface is subject to surface reactions and scavenging by other species [e.g., nitric oxide (NO)} emitted during the night. As a result of nighttime atmospheric stability, ozone transported aloft does not come into contact with scavengers emitted during the night. Thus, overnight advection of ozone aloft is the more significant mechanism of transport from one urban area to another (EPA, 1977; and Chan, et al, 1979).

Control strategies designed to attain and/or maintain the ozone standard in individual urban areas must take into consideration the impact of transported ozone on peak afternoon concentrations.*

A. Present Transport of Ozone at the Surface

The chief impact of ozone transport near the surface is expected to be the more rapid conversion of NO to NO_2. Several field studies have shown

---

*Recall the discussion in Section 3.1, there are days when transport is the predominant cause of observed O_3. The recommendations in Section 3.2.6 apply for instances in which this is not the case.

ALTERNATIVE PROCEDURE FOR ESTIMATING EFFECTIVE STACK HEIGHT

1. Estimate wind speed at stack height

$$u = 5.0 \left[\frac{h}{10} \right]^{.25} \text{ m/s}$$

where: h is the physical stack height in meters

2. Estimate F (the flux parameter)

$$F = g \ V_s \ d^2 \ \ DT/4T_s$$

where: $g = 9.8 \text{ m/s}^2$

V_s = stack gas velocity (m/s)

d = inner stack exit diameter (m)

$DT = T_s - T$ (stack gas temperature-ambient air temperature) °K

T_s = ambient air temperature °K (assume 297°K)

3. Estimate crossover temperature DT_c

For $F < 55$ $\quad DT_c = 0.0297 \ T_s \ V_s^{1/3}/d^{1/3}$

For $F \geq 55$ $\quad DT_c = 0.00575 \ T_s \ V_s^{2/3}/d^{1/3}$

where: T_s = ambient temperature (°K)

V_s = stack gas velocity (m/s)

d = stack exit diameter (m)

If $DT < DT_c$ Go to step 4

If $DT \geq DT_c$ Go to step 5

4. Estimate momentum plume rise

$$Dh = 3\ d\ V_s/u$$

where: d = stack exit diameter (m)

V_s = stack gas velocity (m/s)

u = wind speed at stack height (m)[from Step 1]

Dh = plume rise (m)

Go to Step 6

5. Estimate buoyant plume rise

For $F < 55$ $\qquad Dh = 21.425\ F^{.75}/u$

For $F \geq 55$ $\qquad Dh = 38.71\ F^{.6}/u$

where: Dh = plume rise (m)

F = flux parameter [from Step 2]

u = wind speed at stack height (m)[from Step 1]

6. Estimate effective stack height

$$H = h_s + Dh$$

where: H = effective stack height (m)

h_s = physical stack height (m)

Dh = plume rise (m) [from Step 4 or 5] that ozone transported along the surface tends to be minimal (Chan, et al, 1979; Decker, et al, 1977; and Ludwig, 1979).

Recommended Procedure: Based on the previous discussion, it is recommended that, for most situations, the value for present ozone transported at the surface be set equal to zero for each day modeled.

Alternate Procedure: If ozone levels are measured downtown during 6-9 a.m., surface ozone transport may be considered. It is recommended that the 6-9 a.m. LCT average ozone concentration at an urban site(s) be used as the estimate of the concentration of ozone transported into the urban area along the surface for the given day.

B. Present Transport of Ozone Aloft

As noted above, it appears that unscavenged ozone transported aloft is likely to have a far greater impact than surface transport on maximum afternoon ozone levels observed within or downwind from cities. Thus, estimates of ozone aloft are needed for control strategy development with OZIPM4/EKMA. Techniques for estimating the level of ozone transported aloft have been the subject of two studies (Chan, et al, 1979; and Eaton, et al, 1979). Five different techniques, which were considered to be feasible, were field tested in Philadelphia during the summer of 1978 (Chan, et al, 1979). The five methods are: (1) use of fixed ground based stations; (2) use of airborne measurements in a dedicated aircraft; (3) use of airborne measurements with a portable instrument package; (4) use of free lift balloon soundings; and (5) use of soundings by tethered balloon. Chan, et al (1979), contains a detailed description of each of these techniques as well as a discussion of the findings of the study. Of the five measurement techniques evaluated, surface measurements at fixed sites, airborne measurements by dedicated instrumented aircraft, and soundings by ozonesonde beneath a free balloon were judged to be practical means of providing information on ozone transported aloft.

During the summers of 1985 and 1986, measurements of ozone aloft were made over six cities using aircraft. Cities involved in this analysis were: Dallas, Texas; Tulsa, Oklahoma; Atlanta, Georgia; Birmingham, Alabama; Philadelphia, Pennsylvania; and New York, New York. Ninety percent of the ozone aloft values from this study fall between approximately 25 to 60 ppb. [Baugues, 1987]. Thus, measurements at other sites should be near this range. For those cities located in the ROMNET domain, an alternative procedure is being developed. Present and future aloft values for NMOC, NO_x, CO and O_3 will be based upon results from the ROMNET simulations. Exact procedures and data bases will be available in mid-FY-90.

Recommended Procedure: In selecting this recommendation, consideration has been given to such factors as technical capability and available funding, and the intended use of the data. Ozone measurements taken on the day being modeled are recommended as the best estimate of ozone aloft. These measurements should be obtained at surface monitoring sites upwind of the city during the first hour after breakup of the nocturnal inversion. An acoustic radar (sodar) can be used to determine the time of inversion breakup for the day. If the time of the breakup of the nocturnal radiative inversion is not known, the 1000-1200 Local Civil Time average ozone concentration recorded at the upwind monitor should be used as the transport estimate. A major advantage of surface measurements is that it is the only method which provides continuous measurements and, thus, assurance that measurements exist for days or for times of day which are later determined to be of interest. The site(s) should be located in as rural a location as possible so as not to be appreciably affected by local sources of precursors. The distance such upwind sites should be located from a city depends on the extent of urban development. Because it is desirable not to measure pollutants which are recirculated from the city under review, a distance of 40 km or more upwind from the urban core should be sufficient. This distance perhaps could be reduced for smaller cities. Figure 3-3 depicts orientations for acceptable upwind sites.

Alternate Procedure: Information on the vertical distribution of ozone transported above the surface layer in the early morning may be used directly if it is available. Such information might include aircraft or free-lift ozonesonde measurements. The reader is referred to Chan, et al, 1979, for a detailed discussion of these techniques. Use of an alternate procedure is subject to the approval of the EKMA contact person in the appropriate U. S. EPA Regional Office.

Missing Data: In the event that an estimate of transport is not available for a given day being modeled, the median transport value from the remaining days being modeled should be used as a default value. This procedure applies to all the data gathering techniques described above: fixed site, aircraft, and ozonesonde observations.

C. Future Transport of Ozone

If control programs are implemented in upwind areas, ozone transported into the city may be reduced. However, in most cases, the source area and the level of future controls are not likely to be known to any degree of certainty.

Recommended Procedure: Because of the considerable uncertainty in the location and future control levels of the source area(s) for ozone transported into the urban area, the relationship depicted in Figure 3-4 is recommended for estimating the future ozone transport level given the level of present transport. The solid curve in Figure 3-4 was derived on the basis of changes in VOC emissions which are projected assuming a national mix of source categories; national estimates of projected growth in stationary source emissions and vehicle miles traveled; anticipated impact of applying reasonably available control technology to stationary sources and the impact of the Federal Motor Vehicle Control Program on mobile sources; and consideration of natural background levels. It was assumed that future ozone levels would not exceed the NAAQS. The solid curve is most appropriate for use by cities subject to impacts from large upwind nonattainment areas. The dashed curve is most appropriate for use when a city is isolated and not impacted by large designated nonattainment areas.

Future ozone transport levels can be computed by use of the following equations:

For areas with large designated nonattainment area upwind:

$$O_3 \text{ (future)} = 0.7 * (O_3 \text{ (present)} - 0.04) + 0.04$$

For isolated areas:

$$O_3 \text{ (future)} = 0.9 * (O_3 \text{ (present)} - 0.04) + 0.04$$

Where:

O_3 (future) = future ozone transport level (ppm)

O_3 (present) = present ozone transport level (ppm)

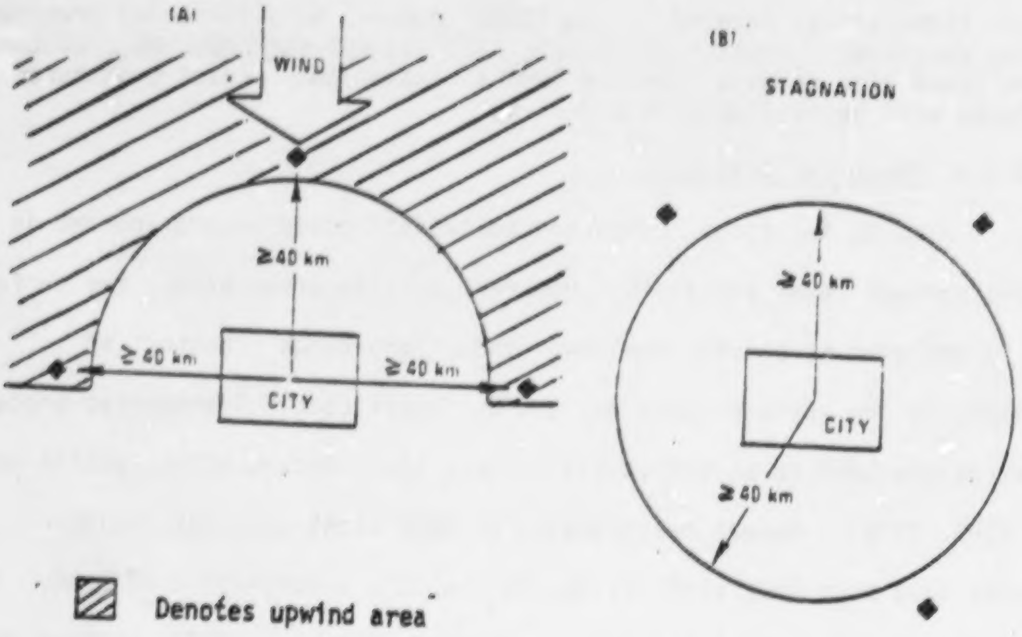
(A)
WIND
≥40 km
≥40 km
≥40 km
CITY
(B)
STAGNATION
≥40 km
CITY
≥40 km
▨ Denotes upwind area

Figure 3-3 Examples of acceptable monitoring locations for estimating transported ozone.

The coefficients "0.7" and "0.9" in the preceding expressions were obtained by reviewing OZIPM4 runs with varying conditions. The preceding expressions assume an irreducible background component of 0.04 ppm.

Without information to the contrary, future transport along the surface should be assumed equal to zero. If significant nonzero concentrations are found for present ozone transport along the surface, then future ozone transport levels should be obtained using the relationships shown in Figure 3-4.

For those cities located in the ROMNET domain, an alternative procedure is being developed. Present and future aloft values for NMOC, NO_x, CO and O_3 will be based upon results from the ROMNET simulations. Exact procedures and data bases will be available in mid-FY-90.

3.2.6 Precursor Transport

Just as for ozone, precursor pollutants could be transported in both the surface layer and aloft. However, outside urban areas, the surface layer is expected to be very shallow. Thus, long-range transport of precursors in the surface layer may not be significant. Transported precursor concentrations tend to be substantially less than concentrations within urban areas (EPA, 1978). Recent measurements of NMOC aloft over six cities indicates that most NMOC aloft values fall within a range of 0-50 ppbC. The overall median value for these data is 30 ppbC [Baugues, 1987]. Future NMOC aloft should be reduced 20 percent from present levels. Present and future levels of NO_x aloft should be set to 2 ppb (.002 ppm). Surface levels of NMOC and NO_x for both present and future conditions should be set to zero.

Carbon monoxide levels at the surface should be set to zero. Concentrations aloft should be set to 0.5 ppm. Future levels of aloft CO may be reduced 20 percent from present levels. For those cities located in the ROMNET domain, an alternative procedure is being developed. Present and future aloft values for NMOC, NO_x, CO and O_3 will be based upon results from

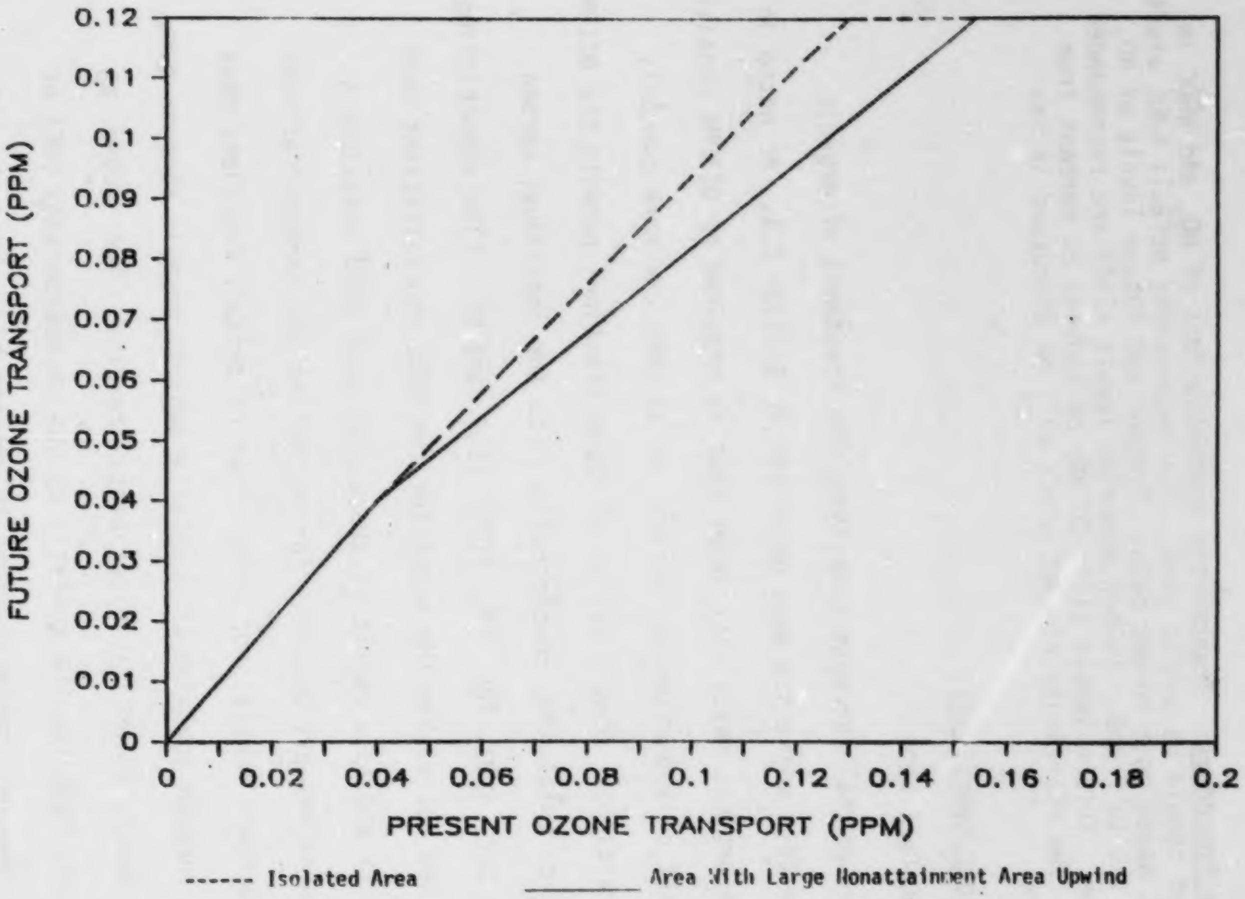

FIGURE 3- 4

FUTURE OZONE TRANSPORT AS A FUNCTION OF PRESENT TRANSPORT the ROMNET simulations. Exact procedures and data bases will be available in mid-FY-90.

Recommended Procedure: Transported concentrations of NO_x and NMOC in the surface layer should be set to zero. The recommended default NMOC aloft value is 30 ppbC based upon recent data. Present and future levels of NO_x aloft should be set to 2 ppb. Carbon monoxide levels aloft are recommended to be set to 0.5 ppm. Future levels aloft CO may be reduced 20 percent from present levels. The reactivity of NMOC aloft will be discussed in the following section.

3.2.7 Organic Reactivity

A. Surface NMOC

The fundamental concepts underlying the treatment of organic reactivity in the CB-4 mechanism were described in Section 2.1. As noted in that section, the organic reactivity input that is required by OZIPM4 consists of specifying a set of apportioning factors, or as they are more commonly termed, carbon-fractions. Specification of these fractions permits the OZIPM4 program to apportion total NMOC concentration into the individual carbon groups--PAR, ETH, OLE, ALD2, TOL, XYL, FORM, ISOP, and NR. (The apportioning procedure is carried out within the model for the NMOC concentrations that occur both initially and as a result of subsequent post-0800 emissions.)

Two basic approaches are possible for estimating the carbon-fractions. The recommended approach consists of using a set of default fractions that have been derived through analyses of available ambient organic species data, and review of pertinent, scientific experimental results. The second, an alternative approach, requires the analysis by gas chromatography (GC) of individual organic species' concentrations in ambient air within the city under review. Typically, this latter approach requires a special field study.

The recommended approach of using a default value rather than making a city-specific determination arises primarily as a consequence of two factors. First, the default values are estimated to be representative of typical urban reactivity based on an analysis of ambient sampling results conducted in a number of locales (Jeffries, 1987). While some city-to-city variations in organic composition are to be expected, the default recommendations should adequately represent most United States cities (Jeffries, 1987). The second factor relates to the resource requirements associated with the alternative approach. The cost of conducting a special ambient sampling program can be substantial.

Instead of using default values, carbon-fractions can be computed from GC analysis of ambient samples. Monitoring considerations in performing GC sampling/analysis are discussed by Singh (1980) and EPA (1980), and will not be repeated here. However, it should be noted that GC analysis is not an automated technique, and is most often done on a special study basis. Thus, a monitoring program of limited duration is the most pragmatic approach for developing the information needed to compute carbon-fractions. While it is difficult to prescribe exactly the number of samples needed, enough should be analyzed to ensure that representative, average carbon-fractions can be computed. Since the carbon-fractions will be used to apportion initial concentrations and concentrations due to fresh emissions, the most appropriate sampling period is one prior to the onset of significant photochemical reaction. As with NMOC monitoring, sampling during the 6-9 a.m. time period within the area of maximum emission density (i.e., usually the center city) is generally recommended. Ambient samples for GC analysis should be collected by integration over a period of 3 hours.

The GC analysis must identify all species up to and including C-12 (compounds containing 12 carbons). Identification of any peak over 0.5 parts per billion (ppbC) is required. Where an individual peak cannot be identified as a specific compound, it must be analyzed to determine the carbon number and the class (paraffin, olefin, or aromatic).

Regardless of the technique employed in their derivation, the carbon-fractions are used to apportion total concentrations of organic compounds which are based upon ambient measurements. Of the two organic compound monitoring techniques [i.e., PDFID (preconcentration direct flame ionization detection) and GC], both rely on a flame ionization detector that is relatively inefficient in responding to many oxygenated compounds such as aldehydes and ketones (i.e., these techniques measure hydrocarbons only). SAI has estimated that, initially, total carbonyl compounds (i.e., those including aldehyde and ketones, as well as some surrogate carbonyls) are about 5 percent of total nonmethane hydrocarbon concentrations (Killus and Whitten, 1983). Only about 1 percent of the total carbon that is measured can be classified in the carbonyl group (i.e., surrogate carbonyls). The remainder of the carbonyls (i.e., 5 percent of the nonmethane hydrocarbons that are measured) is attributable to oxygenates that are not detected. The carbon-fractions which would sum to 1.05 (or 105 percent) are then adjusted so that they total only 1.00 or 100 percent. If ambient measurements of aldehydes are available, a city-specific determination of the carbonyl fraction can be made. However, these measurements tend to be complex, using techniques that are mostly conducted by research groups. As a consequence, carrying out a special aldehyde monitoring program cannot be routinely recommended.

Whenever city-specific estimates are made by the techniques discussed above, special care must be taken to ensure that the computed carbon-fractions represent a realistic distribution of NMOC species.

Reactivities of NMOC in numerous cities have been computed based upon K_{OH} values. K_{OH} values are rate constants which give a measure of the reactivity of a class of compounds with OH radicals. The weighted sum of these K_{OH} values give an estimate of the overall reactivity of the NMOC mix.

The K_{OH} value for an NMOC mix can be determined using the following equation:

$$\overline{K_{OH}} = PAR * 1203 + ETH * 5824 + OLE * 20422 + ALD2 * 11833 + TOL * 1284 + XYL * 4497 + FORM * 15000$$

Where: $\overline{K_{OH}}$ is the average K_{OH} value for the NMOC mix, PAR is the fraction of the mix considered paraffin (based upon the CB-4 splits).

A typical city is expected to have an average K_{OH} value that falls between 2700 and 3600 min^{-1}. If the computed K_{OH} value, based upon a city-specific NMOC distribution, does not fall within this range, the process of determining the city-specific distribution should first be redone to check for errors. If no errors are found, the default reactivity should be utilized.

Requests to use reactivities other than the default must be reviewed and approved by the appropriate Regional Office in cooperation with the Model Clearinghouse.

Recommended Procedure. The carbon-fractions recommended for use in an EKMA/CB-4 analysis are listed below:

PAR = .564
ETH = .037
OLE = .035
ALD2 = .052
FORM = .021
TOL = .089
XYL = .117
ISOP = 0
NR = .085

They should normally be used unless sufficient information is available to derive city-specific information by the method discussed below.

Alternate Approach. If analyses of ambient air samples by gas chromatography are available for a particular city, the results can be used to derive carbon-fractions. The ambient samples should be taken in the high emission density area (normally the urban core) within the 6-9 a.m. Local Daylight Time (LDT) period during the ozone season. Integrated samples are required. It is desirable that enough samples be analyzed to provide a representative average. For supplemental information regarding monitoring aspects, the reader is referred to Singh (1980) and Rhoads (1987), and for details on how carbon-fractions are computed from the sampling results, the reader is referred to Appendix C of this document. Those considering this approach should discuss it with the EKMA contact in the appropriate Regional Office.

Caveat. If the alternative approach is used, the resultant reactivity must fall within the range of 2700-3600 min^{-1}. If it does not, it is strongly recommended that the data and computations be thoroughly checked to ensure that no errors have been introduced. If the problem cannot be resolved, use of the default carbon-fractions listed in the recommended procedure above is preferable.

B. NMOC Aloft

OZIPM4 also requires carbon-fractions for the NMOC aloft. The recommended approach is to use the default value provided. These values are based upon GC speciation of aircraft samples taken over six cities during the summers of 1985 and 1986 [Baugues, 1987]. In order to develop a city-specific distribution, a special field study would be required. Such an analysis is not recommended.

For those cities located in the ROMNET domain, an alternative procedure is being developed. Present and future aloft values for NMOC, NO_x, CO and O_3 will be based upon results from the ROMNET simulations. Exact procedures and data bases will be available in mid-FY-90.

Recommended Procedure. The carbon-fractions recommended for use in EKMA/CB-4 for NMOC aloft are:

PAR = .498
ETH = .034
OLE = .020
ALD2 = .037
FORM = .070
TOL = .042
XYL = .026
ISOP = 0
NR = .273

3.2.8 Temperature

Hourly temperature data must be utilized in OZIPM4. Use of hourly temperatures allows reaction rates to be increased or decreased according to the hourly temperature. If not specified, OZIPM4 uses a default temperature of 303°K. The hourly surface temperatures to be utilized in OZIPM4 should be from an urban meteorological station. Tapes which provide complete hourly data are available from the National Oceanic and Atmospheric Administration (NOAA) in Asheville, NC.

Recommended Procedure. Hourly surface temperatures from an urban meteorological station are recommended for use in OZIPM4.

3.2.9 Water Vapor

Recent work has shown that ozone predictions are sensitive to the amount of atmospheric moisture content. A new option has been included in OZIPM4 which will estimate the atmospheric moisture content given relative humidity values and an ambient pressure level. Hourly values of relative humidity can be found on meteorological tapes available from NOAA (in Asheville, NC).

Recommended Procedure. Hourly relative humidity values are recommended for use in OZIPM4.

3.2.10 Biogenic Emission Estimates

OZIPM4 has recently been modified to contain an option to allow inclusion of biogenic emission rates. The inputs to OZIPM4 are emission estimates of the biogenics, typically broken out as: isoprene, a-pinene, monoterpenes and unknowns. The units for these values are kilograms per square kilometer per hour ($kg/km^2/hr$).

The biogenic emission estimates are sensitive to several meteorological parameters: air temperature, wind speed, relative humidity and cloud cover. Therefore, biogenic emission estimates must be developed for each day modeled and the values based upon day specific meteorological parameters.

EPA will provide a computer program that can be run on an IBM-PC (or compatible machine) which will estimate biogenic emissions rates on a county basis. The user would need to provide day specific meteorological parameters. This program should be available by mid-1990.

As with man-made emissions (Section 3.2.3), emission rates should be included for the county in which the straight line trajectory is over for each hour.

OZIPM4 also requires initial values for biogenic species. All initial values should be set to 0.0001 ppm in the absence of measured concentrations. They should not be left at zero, as this may cause the program to "hang up".

3.3 Predicting Peak Ozone

In one study, it was found that EKMA could yield a lower control estimate for a case when peak ozone is underpredicted as compared to one in which peak ozone is more accurately predicted (Jeffries, et al, 1981). In extreme cases of underprediction, a solution may not be possible with EKMA. In a similar fashion, a large overprediction could lead to a control estimate that is higher than that obtained when good agreement is found. As part of the supplemental EKMA guidance issued in December of 1981, EPA addressed this problem by recommending that predictions of peak ozone be made, and appropriate adjustments or compensations be made if poor agreement is found (Rhoads, 1981). In this section, the procedures for making the predictions, comparing them with observations, and making appropriate adjustments are described.

3.3.1 Procedures for Making Ozone Predictions

In Section 3.2, most of the OZIPM model inputs that are needed either to predict peak ozone or to estimate VOC emission reductions were discussed. In order to make predictions of peak ozone, one additional set of model input variables is needed: the concentrations of NMOC, NO_x, and CO that are representative of the initial (i.e., 8 a.m.), urban core levels. These model inputs are the most critical for making predictions, and should be estimated on a case-by-case basis. Because of the model sensitivity to these inputs, use of mean or median values compiled from measurements taken across a number of days may lead to erroneous results. Thus, day-specific measurements should normally be used to make these estimates.

As for estimating the initial concentrations, the recommended procedure is to make use of ambient NMOC, NO_x, and CO measurements routinely taken in the urban core, but which represent neighborhood scale levels. The initial concentrations are intended to represent the NMOC, NO_x, and CO that is initially present within the mixed layer at the start of the model simulation (i.e., 8 a.m.). While several approaches could be taken, the recommended method is to use the 6-9 a.m. average concentration measured by collocated NMOC, NO_x, and CO monitors within the urban core which represent neighborhood scale values. If more than one set of measurements are available from several such monitors, then the 6-9 a.m. average concentration at each monitor should be averaged to obtain an overall, urban average NMOC, NO_x, and CO concentration. Algebraically, the above procedure can be expressed as follows:

$$C_{(NMOC)o} = \frac{\sum_{i=1}^{n} \left[C_{(NMOC)6-9} \right]_i}{N} \qquad (3\text{-}4a)$$

and

$$C_{(NOx)o} = \frac{\sum_{i=1}^{n} \left[C_{(NOx)6-9} \right]_i}{N} \qquad (3\text{-}4b)$$

and

$$C_{(CO)o} = \frac{\sum_{i=1}^{n} \left[C_{(CO)6-9} \right]_i}{N} \qquad (3\text{-}4c)$$

where

$({}^{C}NMOC)o$, $({}^{C}NO_x)o$, $({}^{C}CO)o$ = initial concentrations of NMOC, NO_x, and CO (in units of ppmC, ppm, and ppm, respectively) input to OZIPM4 simulation

$[({}^{C}NMOC)6\text{-}9]i$, $[({}^{C}NO_x)6\text{-}9]i$ $[({}^{C}CO)6\text{-}9]i$ = the 6-9 a.m. average concentrations of NMOC, NO_x, and CO (in units of ppmC, ppm, and ppm, respectively) taken in the urban core (or high emission density area) at site i

N = total number of collocated monitors for which day-specific NMOC and NO_x measurements are available.

As noted above, the initial NMOC and NO_x concentrations are derived from day-specific measurements of NMOC and NO_x. In some instances, an NMOC measurement may not be available for the day being modeled. In such a case, the initial NMOC concentration can be approximated by making use of the median $NMOC/NO_x$ ratio (see Section 3.4.3) and a day-specific measurement of NO_x alone, provided it is available. The initial NMOC concentration for use with the OZIPM4 simulation can be computed as the product of the median $NMOC/NO_x$ ratio and initial NO_x concentration, or

$$({}^{C}NMOC)o = ({}^{C}NO_x)o\ (NMOC/NO_x) \qquad (3\text{-}5)$$

where

$({}^{C}NMOC)o$ = the initial NMOC concentration for the OZIPM4 simulation, ppmC

$({}^{C}NO_x)o$ = the initial NO_x concentration calculated by equation 3-4b, ppmC

$(NMOC/NO_x)$ = the median $NMOC/NO_x$ ratio as derived according to the procedures outlined in Section 3.4

It should be emphasized that this approach is an approximation, and the one described in the preceding paragraph is preferable.

With the estimates of initial NMOC, NO_x, and CO, and the corresponding day-specific inputs listed in Table 3-1, the CALCULATE option of OZIPM4 may be used to perform a single model simulation. An example simulation and additional information are contained in EPA, 1989. Thus, no additional discussion will be included here.

Recommended Procedure. The CALCULATE option of the OZIPM4 program should be used to predict peak ozone for comparison with the observed peak. The model inputs discussed in Section 3.2 should be used, with initial concentrations that have been derived according to equations 3-4a, 3-4b, and 3-4c, using data that are specific to the day being modeled. In the event that day-specific NMOC measurements are unavailable, the initial NMOC concentration can be approximated by means of equation 3-5, with the recognition that some uncertainty may be introduced in the analysis. If day-specific measurements of NMOC, NO_x, and CO are not available, predictions of peak ozone cannot be made. In this case, computation of VOC control estimates are recommended, but without the requirement of reasonable agreement between prediction and observation.

3.3.2 Comparisons of Predictions With Observations

The principal output of concern obtained with a CALCULATE simulation is the predicted ozone. By numerically integrating the differential equations describing ozone formation processes (i.e., chemical reaction, emissions, dilution, etc.), instantaneous concentrations of ozone are computed throughout the simulation period. From this computed profile of instantaneous ozone concentrations, the OZIPM4 program calculates the hourly average concentrations occurring during the model simulation. The predicted ozone concentration that occurs at the time of the observed peak is used in the performance measure that is recommended to evaluate model performance. This performance measure is the relative deviation of the prediction from the observation, or

$$\mathrm{DEV} = \frac{C_p - C_o}{C_o} \times 100 \qquad (3\text{-}6)$$

where

DEV = deviation of the model prediction from the observation, percent

C_p = maximum 1-hour average predicted peak ozone, ppm

C_o = observed peak ozone, ppm

If the relative deviation is found to be no more than ± 30 percent, then agreement between the prediction and the observed peak is judged to be sufficient to proceed with control estimate calculations. If the deviation is outside the ± 30 percent range, a comparison between the measured peak and predicted peaks 1 hour before (or after) the time of the observed peak should be made. Due to the uncertainty in trajectories, it is possible for the time of the predicted peak to be off by an hour.

If the model underpredicts by more than 30 percent (i.e., DEV < - 30 percent) or overpredicts by more than 30 percent (i.e., DEV > + 30 percent), the review of, and possible adjustment to, key model inputs according to the discussion of Section 3.3.3 below is warranted. It should be noted that the observed ozone peak (not the predicted) is recommended for subsequent control calculations.

Recommended Procedure. The relative deviation of the model prediction from the observed peak should be computed according to equation 3-6 above. The model predicted peak to be used in this computation is the hourly average ozone concentration calculated by the OZIPM4 program at the time of the observed peak. If the computed deviation is within ± 30 percent, then the model results are sufficiently accurate for control estimate calculations. If the deviation is outside the ± 30 percent envelope comparisons between the measured peak and the predicted values 1 hour before (or after) the time of the measured peak should be made. If the ± 30 percent test is not met, then the procedures discussed in Section 3.3.3 should be applied in an attempt to improve the simulation results.

3.3.3 Review and Adjustment to Model Inputs

If inadequate agreement between a model prediction and an observed peak is found, review of the model inputs should be conducted. The objective of this review is to investigate whether some modifications to key model inputs can be justified on some physical basis in order to improve the model predictions. This review should focus on those model inputs that most critically affect predictions of peak ozone. Of most importance are the initial NMOC, NO_x, and CO concentrations; dilution; and post-0800 emissions. Adjustment of these inputs, within the uncertainties associated with their development, is warranted if improvements in model predictions can be made. Obviously, any errors that may have been made in their derivation should be corrected as well.

While specific recommendations in trouble-shooting poor model performance are difficult to make, some general guidelines can be made depending on the nature of the problem, be it an underprediction or an overprediction. If some uncertainty exists with regard to the data from which they were derived, then the inputs can be adjusted within that range of uncertainty. In general, initial NMOC, NO_x, and CO levels may be adjusted by ± 15 percent and maximum afternoon mixing height by ± 200 meters (Seila, 1986 and Rhodes and Evans, 1986). Outliers in the data may be deleted if adequate justification is available. For example, assume that an initial NMOC concentration had been derived from 6-9 a.m. measurements taken at three monitoring sites. However, the 6-9 a.m. concentration at one site (say site A) deviated substantially from the concentrations measured at the other two sites (say sites B and C). Then, improved agreement between model predicted and observed ozone might be found if the initial NMOC concentration for the day in question was derived solely from the measurements taken at the two sites in agreement (i.e., sites A and B). Consider the case of underprediction first. The following steps should be taken:

1. Check inputs for errors (especially morning and afternoon mixing heights and ozone aloft).

2. Increase the initial NMOC, NO_x and CO concentrations by 15 percent.

3. Reduce afternoon mixing height by 200 meters.

4. Increase original afternoon mixing height by 200 meters (may improve situations where ozone aloft is high).

5. Increase morning mixing height by 50 meters.

All steps are cumulative, except for 3/4, where the step that improves the situation should be included with Step 5. Steps are to be followed in the order above, and carried out only until the deviation is within the ± 30 percent range. Further adjustments should not be carried out to reduce the deviation.

When changes are made to the morning mixing height, make sure that changes are reflected in all options. The following options use the morning mixing height: DILU (Dilution), MASS (Emissions), CRED (CO) and BIOG (Biogenics).

Guidelines for correcting a problem of overprediction are similar in concept to those for underprediction. The following steps should be taken:

1. Check inputs for errors (especially morning and afternoon mixing heights and ozone aloft). Also make sure that all emission rates are being read in as $kg/km^2/hr$ and not in fractions of the initial concentration.

2. Reduce initial NMOC, NO_x and CO concentrations by 15 percent.

3. Increase afternoon mixing height by 200 meters.

4. Reduce original afternoon mixing height by 200 meters (may improve cases where ozone aloft is high).

5. Reduce morning mixing height by 50 meters.

The same rules apply that were described earlier for the underprediction case.

As noted above, the model inputs that substantially affect model predictions of peak ozone include the initial NMOC, NO_x, and CO concentrations, and initial mixing height. The possibility exists that mass balance techniques could be used to evaluate the appropriateness of a particular set of initial concentrations and an initial mixing height. For example, one could test by means of a simplified box model whether or not a city's emissions are sufficient to generate the measured initial concentrations within a mixed layer corresponding to the postulated initial mixing height. While such an approach is intuitively appealing, such calculations may not be able to account properly for ventilation, and for advection of pollutants from source areas nearby the precursor monitors. Nevertheless, it does provide one means of assessing the reasonableness of the postulated model inputs.

Recommended Procedure. To improve agreement with observed O_3 levels, model inputs can be varied within reasonable ranges if justification for doing so can be cited. Specifically, the key model inputs are initial NMOC, NO_x, and CO concentrations, and mixing heights. Finally, model inputs should only be adjusted within the range of reasonable uncertainty, and not just selected such that good agreement between the model prediction and observed peak is obtained. Finally, if acceptable agreement cannot be found, control estimates should still be made and the procedures discussed in Section 3.5 applied.

3.4 Computing VOC Emission Reductions

The recommended procedure for computing VOC emission reductions is to use the EKMA option in OZIPM4. Use of this option eliminates the need to generate isopleth diagrams. OZIPM4 performs the necessary calculations and determines the VOC emission reduction. Several variables are needed to perform this calculation. These include: initial NMOC, initial NO_x, initial CO, NMOC/NO_x ratio, maximum observed ozone, present and future levels of NMOC aloft, NO_x aloft, O_3 aloft, and assumptions regarding future levels of NO_x and CO. Use of this option is discussed further in EPA, 1989.

3.4.1 Derivation of Empirical Data

Two pieces of empirical data are needed for calculating control requirements. The first is the maximum 1-hour average ozone concentration observed at the site of interest. The degree of emission control necessary to reduce this "peak" to 0.12 ppm is to be calculated; hence, the peak level will be termed the daily site-specific ozone maxima.

The second piece of information needed is the NMOC/NO_x ratio. This ratio is derived from the 6-9 a.m. concentrations of NMOC and NO_x within the urban area. The ratio will be termed the design ratio. The procedures for deriving both the daily site-specific ozone control values and the design ratios are described below.

3.4.2 Daily Site-Specific Ozone Control Value

The daily site-specific ozone maxima is used in conjunction with the NMOC/NO_x ratio for calculating control estimates needed to reduce the day-specific and site-specific observed peak ozone to 0.12 ppm. The daily ozone maxima should be expressed in ppm units rounded to two decimal places.

Recommended Procedure: A daily site-specific ozone maxima is obtained for each site which is downwind of the city, and/or within the city in the case of light and variable winds on the day for which the control strategy is to be developed. Surface wind data should be examined to assure that the site is not "upwind" of the city. Based on the results of field studies and reviews in which ozone gradients downwind from urban areas were examined, peak ozone concentrations should generally be observed within 15-45 km downwind of the central business district (EPA, 1978; Martinez and Meyer, 1976; and EPA, 1976).

3.4.3 NMOC/NO_x Ratios

The prevailing 6-9 a.m. LCT NMOC/NO_x ratio measured in the urban core of the city is the second piece of empirical data required. The design ratio is viewed as characteristic of the city which would prevail during the remainder of the morning and early afternoon in the absence of chemical reactions. OZIPM4 expresses peak ozone concentrations as a function of the initial concentration of NMOC and NO_x. Thus, the 6-9 a.m. LCT NMOC/NO_x ratio is considered to be the appropriate ratio for use in OZIPM4 since this ratio is consistent with the conceptual basis of the model (Dimitriades, 1977). To ensure that representative ratios are obtained, the NMOC and NO_x instruments should be collocated in the central core of the urban area. The site(s) should be located in an area of relatively uniform emission density and not significantly influenced by any individual source. More detailed guidance on siting NMOC instruments is contained in EPA, 1980. Guidance on the operation of NMOC instruments is available in EPA, 1985.

Significant discrepancies have been found between NMOC/NO_x ratios calculated on the basis of ambient measurements and those obtained from emission inventory data (Drivas, 1978). Reasons for the lack of correlation between the two ratio calculation procedures have not been resolved. As a result, only ambient NMOC/NO_x ratios should be used with EKMA since these ratios are consistent with the conceptual basis of the model and the emission ratios have been shown to be poor surrogates for these ambient ratios.

NMOC data analyzed only with the PDFID (preconcentration direct flame ionization detection) or GC (gas chromatograph) should be used with OZIPM4 (Rhoads, 1985). Due to the large uncertainty in low NO_x values, any day with a 6-9 a.m. NO_x concentration at or below 0.020 ppm should be excluded from the process of estimating $NMOC/NO_x$ ratios.

The NMOC data are to be collected during the season of peak ozone concentrations (summer). Because NMOC concentrations are apt to be relatively high in central urban locations at those times of the day (early morning) when these measurements are required for use in EKMA more confidence can be placed in the estimate. Because of the variability in individual NMOC readings, the $NMOC/NO_x$ ratio calculated for a single day is not recommended for use in city-specific EKMA. Considering instrument reliability and model sensitivity, the following procedure is recommended for calculating $NMOC/NO_x$ ratios.

Recommended Procedure:

1. Individual $NMOC/NO_x$ ratios at a site are calculated as the ratio of the 6-9 a.m. LCT average NMOC and NO_x concentrations, i.e., the average of the hourly concentrations for hours 6-7, 7-8, and 8-9 LCT, respectively. Ratios should not be calculated for any day with less than two valid hours for either NMOC or NO_x.

2. If precursor measurements from more than one urban site are available for the same day, all NMOC and NO_x measurements should be averaged for the day. The $NMOC/NO_x$ ratio is then found by dividing the average NMOC level by the average NO_x value.

3. The peak ozone level for all days with $NMOC/NO_x$ ratios is determined. For isolated cities this is fairly straightforward. All ozone monitors in the Metropolitan Statistical Area are reviewed and the peak values chosen. If the area is subject to transport, site days which may be experiencing transport should be analyzed using procedures outlined in Meyer and Baugues (1989).

4. Once the local ozone peaks have been determined for all days with NMOC/NO_x ratios, the highest ozone days are selected. This consists of either all days with ozone peaks above the NAAQS or the top 10 days if less than 10 days exceed the NAAQS.

5. The days selected in Step 4 are then ranked and a median NMOC/NO_x ratio determined.

It is the median NMOC/NO_x ratio that is to be utilized in OZIPM4. Two examples of calculating a median NMOC/NO_x ratios are shown in Table 3-2.

3.5 Selection of the VOC Emission Reduction Target

3.5.1 Without "Overwhelming" Transport

After all site/day combinations have been modeled, the final step of the modeling analysis involves the selection of the overall VOC emission reduction target. In essence, this procedure is dictated by the form of the ozone NAAQS, and is identical to the method recommended in the March 1981 guidelines document (Gipson, 1981). In summary, a control target is selected for each site that permits, on average, one hourly-average concentration above 0.12 ppm per year. This corresponds to selecting the fourth highest control level if 3 valid years of data are available, the third highest control for 2 years of data, and the second highest control estimate for only 1 year.* The overall control target is then chosen as the highest of the site-specific control estimates to ensure that the ozone standard is attained at all sites.

As noted in the March 1981 guidelines, an additional factor that could affect the procedure just described is the consideration of model predictions

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* A site is considered to have a valid year of data if valid daily maxima exist for at least 75 percent of the days during the ozone season and there is no obvious pattern of missing data during periods when maximum ozone is most likely. A valid daily maxima exists if 75 percent of the hours in a day report data and there is no systematic lack of data during times of day when high ozone is most likely. The reader is referred to EPA 1979b and FR (March 19, 1981) for further information.

TABLE 3-2. EXAMPLE CALCULATION OF THE DESIGN NMOC/NO_x RATIO

Example 1

Date	Max O_3 (ppm)	NMOC/NO_x ratio Site 1	Rank	NMOC/NO_x ratio
7/1	.15	6.9	1	5.3
6/2	.15	7.5	2	6.7
7/3	.14	11.3	3	6.9
7/4	.14	14.0	4	7.5
8/5	.14	5.3	5	8.4
8/8	.14	8.7	6	8.7<---Median
7/9	.13	9.2	7	9.2
6/10	.13	6.7	8	9.5
7/11	.13	8.4	9	11.3
9/12	.13	9.5	10	12.1
7/15	.13	12.1	11	14.0

Example 2

Date	Max O_3 (ppm)	NMOC/NO_x ratio Site 1	Rank	NMOC/NO_x ratio
8/1	.16	5.8	1	5.8
7/2	.16	8.4	2	7.8
6/3	.15	12.3	3	7.8
7/5	.14	8.8	4	8.3
8/8	.13	7.8	5	8.4
9/9	.13	7.8	6	8.6<---Median
6/10	.13	8.3	7	8.8
7/11	.12	10.1	8	9.0
6/12	.12	9.0	9	10.1
9/15	.12	8.8	10	12.3

versus observations. Recall from Section 3.3.2 that a VOC emission reduction estimate should not be used when the model predicted peak ozone disagrees with the observed peak by more than ± 30 percent. This does not apply to days which do not have day-specific measurement of NMOC and NO_x. However, it has been observed that substantial underpredictions of base case, peak ozone may lead to control estimates which are too low (Jeffries, et al, 1981). Conversely, significant overpredictions of base case, peak ozone may yield control estimates which are too high. Under some circumstances, this finding enables one to use control estimates for those days in which base case, peak ozone is poorly predicted. To illustrate, consider an example in which model predictions and control estimates have been made for a site with 3 years of ozone data (see Table 3-3). Note that for Day 1, peak ozone is substantially underpredicted, and the control estimate is the highest of all days. If any improvements were made to predicted peak ozone, the control estimate for this day would likely be increased even more. Since the control estimate for Day 1 is already higher than the control target (i.e., 45 percent), any improvements in model predictions would not affect the selection of the final control target. Thus, the results from Day 1 can be used, even though the model significantly underpredicted peak ozone. The converse situation occurs for Day 5. In this case, any improvements in model predictions would likely reduce the control estimate for that day, again having no bearing on the choice of the final control target. If the model prediction is poor, but neither of the situations described above occur (i.e., overprediction and high control estimate, or underprediction and low control estimate), then it is

TABLE 3-3. EXAMPLE ILLUSTRATING EFFECT OF MODEL PREDICTIONS ON SELECTION OF CONTROL TARGET

Day	Observed Ozone, ppm	Predicted Ozone, ppm	Relative[†] Deviation, %	Control Estimate, %	Rank of Control Estimates
1	0.27	0.18	-33	55	1
2	0.22	0.20	- 9	47	3
3	0.20	0.22	+10	51	2
4	0.18	0.18	0	45**	4
5	0.15	0.21	+40	42	5

† Deviation = $\frac{\text{predicted - observed}}{\text{observed}} \times 100$

** Control Target = fourth highest control estimate (for 3 years of data) recommended that the site/day be discarded, and replaced by the day with the next lowest peak ozone concentration.

Recommended Procedure. To obtain the final VOC emission reduction target, site-specific control requirements must first be determined. In general, a candidate control estimate is chosen for each site based on the number of years of data and the statistical form of the ozone standard (i.e., fourth highest control for 3 years, third highest for 2 years, and the second highest for 1 year). Of the candidate site-specific control estimates, the highest one is selected as the overall VOC emission reduction target. However, all cases in which predictions and observations disagree by more than 30 percent, should be discarded, unless:

(1) peak ozone is underpredicted and the VOC reduction estimate is greater than the candidate site-specific estimate;

(2) peak ozone is overpredicted and the VOC reduction estimate is lower than the candidate site-specific estimate.

In the event that a day is eliminated, the next lowest peak at the site in question should be added for modeling.

3.5.2 Selection of a VOC Reduction Target at Sites Subject to Overwhelming Transport

In Section 3.1, we noted that some days initially selected may be discarded (for modeling purposes), if shown to be subject to "overwhelming transport." Nevertheless, a demonstration that the local MSA will attain the NAAQS still needs to be made. Once a day has been discarded for local modeling analysis, a determination needs to be made concerning what MSA/CMSA is most likely responsible for the excluded observed daily maximum. Procedures for doing this are suggested by Meyer and Baugues (1989). These procedures require a review of all surface National Weather Service (NWS) wind data within 100 miles of the monitoring site plus any special study surface wind data collected at properly exposed sites (EPA, 1986). In general, if the wind data suggest an air parcel located at the monitor at the time of the observed maxima may have been within an upwind MSA/CMSA between 8 a.m. to noon, that upwind CMSA/MSA may be instrumental in causing the observed daily maximum. If the discarded day for the local MSA has a daily maximum ozone level higher than that for the fifth highest modeled day for the upwind CMSA/MSA, the discarded day should be included in the upwind CMSA/MSA's modeling analysis. If a discarded daily maxima is included in an upwind MSA/CMSA's analysis, it may be ignored in the local attainment demonstration.

In some cases, however, it may not be possible to identify the upwind CMSA/MSA most likely responsible for an observed daily maximum ozone concentration. If this happens, the event is referred to as an "irreducible exceedance." Presence of one or more irreducible exceedances at a monitoring site has the effect of raising the local VOC control target needed to meet the NAAQS at that site. For example, the site-specific control requirement at a site with three valid years of data would become the third (rather than the fourth) highest control estimate if there were one "irreducible exceedance" at the site. If the particular site-specific control requirement were the highest amongst all the sites assigned to the local MSA, the local MSA's overall VOC reduction target would be similarly affected.

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APPENDIX A

LISTING OF CB-4 MECHANISM

TABLE A-1. CB-4 MECHANISM

	Reaction	Rate Constant at 298°K (ppm^{-1} min^{-1})	Activation Energy (°K)
1.	$NO_2 \rightarrow NO + O$	1.0	0
2.	$O \rightarrow O_3$	4.323×10^{6}	- 1175
3.	$O_3 + NO \rightarrow NO_2$	26.64	1370
4.	$O + NO_2 \rightarrow NO$	1.375×10^{4}	0
5.	$O + NO_2 \rightarrow NO_3$	2309	- 687
6.	$O + NO \rightarrow NO_2$	2438	- 602
7.	$NO_2 + O_3 \rightarrow NO_3$	0.04731	2450
8.	$O_3 \rightarrow O$	0.053	0
9.	$O_3 \rightarrow O1D$	1.0	0
10.	$O1D \rightarrow O$	4.246×10^{5}	- 390
11.	$O1D + H_2O \rightarrow 2OH$	3.26	0
12.	$O_3 + OH \rightarrow HO_2$	100	940
13.	$O_3 + HO_2 \rightarrow OH$	3	580
14.	$NO_3 \rightarrow 0.89\ NO_2 + 0.89\ O + 0.11\ NO$	33.9	0
15.	$NO_3 + NO \rightarrow 2\ NO_2$	4.416×10^{4}	- 250
16.	$NO_3 + NO_2 \rightarrow NO_2 + NO$	0.5901	1230
17.	$NO_3 + NO_2 \rightarrow N_2O_5$	1853	- 256
18.	$N_2O_5 + H_2O \rightarrow 2\ HNO_3$	1.9×10^{-6}	0
19.	$N_2O_5 \rightarrow NO_3 + NO_2$	2.776	1.09×10^{4}
20.	$NO + NO \rightarrow 2\ NO_2$	1.539×10^{-4}	- 530
21.	$NO + NO_2 + H_2O \rightarrow 2\ HNO_2$	1.6×10^{-11}	0

TABLE A-1. CB-4 MECHANISM (CONTINUED)

Reaction	Rate Constant at 298°K (ppm^{-1} min^{-})	Activation Energy (°K)
22. $NO + OH \rightarrow HNO_2$	9799	- 806
23. $HNO_2 \rightarrow NO + OH$	.1975	0
24. $OH + HNO_2 \rightarrow NO_2$	9770	0
25. $HNO_2 + HNO_2 \rightarrow NO + NO_2$	1.5×10^{-5}	0
26. $NO_2 + OH \rightarrow HNO_3$	1.682×10^{4}	- 713
27. $OH + HNO_3 \rightarrow NO_3$	217.9	- 1000
28. $HO_2 + NO \rightarrow OH + NO_2$	1.227×10^{4}	- 240
29. $HO_2 + NO_2 \rightarrow PNA$	2025	- 749
30. $PNA \rightarrow HO_2 + NO_2$	5.115	1.012×10^{4}
31. $OH + PNA \rightarrow NO_2$	6833	- 380
32. $HO_2 + HO_2 \rightarrow H_2O_2$	4144	- 1150
33. $HO_2 + HO_2 + H_2O \rightarrow H_2O_2$	.2181	- 5800
34. $H_2O_2 \rightarrow 2\ OH$	.189	0
35. $OH + H_2O_2 \rightarrow HO_2$	2520	187
36. $OH + CO \rightarrow HO_2$	322	0
37. $FORM + OH \rightarrow HO_2 + CO$	1.5×10^{4}	0
38. $FORM \rightarrow 2\ HO_2 + CO$	1.0	0
39. $FORM \rightarrow CO$	1.0	0
40. $FORM + O \rightarrow OH + HO_2 + CO$	237	1550
41. $FORM + NO_3 \rightarrow HNO_3 + H_2O + CO$	0.93	0
42. $ALD2 + O \rightarrow C_2O_3 + OH$	636	986
43. $ALD2 + OH \rightarrow C_2O_3$	2.4×10^{4}	- 250

TABLE A-1. CB-4 MECHANISM (CONTINUED)

Reaction	Rate Constant at 298°K (ppm^{-1} min^{-1})	Activation Energy (°K)
44. ALD2 + NO_3 --> C_2O_3 + HNO_3	3.7	0
45. ALD2 --> FORM + $2HO_2$ + CO + XO_2	1.0	0
46. C_2O_3 + NO --> FORM + NO_2 + HO_2 + XO_2	1.831×10^4	- 250
47. C_2O_3 + NO_2 --> PAN	1.223×10^4	- 5500
48. PAN --> C_2O_3 + NO_2	.0222	1.4×10^4
49. C_2O_3 + C_2O_3 --> 2 FORM + $2XO_2$ + $2HO_2$	3700	0
50. C_2O_3 + H_2O --> 0.79 FORM + 0.79 XO_2 + 0.79 HO_2 + 0.79 OH	9600	0
51. OH --> FORM + XO_2 + HO_2	21	1710
52. PAR + OH --> 0.87 XO_2 + 0.13 OX_2N + 0.11 HO_2 + 0.11 ALD2 - 0.11 PAR + 0.76 ROR	1203	0
53. ROR --> 0.96 XO_2 + 1.1 ALD2 + 0.94 HO_2 - 2.1 PAR + 0.04 XO_2N + 0.02 ROR	1.371×10^5	8000
54. ROR --> HO_2	9.544×10^4	0
55. ROR + NO_2 -->	2.2×10^4	0
56. O + OLE --> 0.63 ALD2 + 0.38 HO_2 + 0.28 XO_2 + 0.3 CO + 0.2 FORM + 0.02 XO_2N + 0.22 PAR + 0.2 OH	5920	324
57. OH + OLE --> FORM + ALD2 - PAR + XO_2 + HO_2	4.2×10^4	- 504
58. O_3 + OLE --> 0.5 ALD2 + 0.74 FORM + 0.22 XO_2 + 0.1 OH + 0.33 CO + 0.44 HO_2 - PAR	.018	2105
59. NO_3 + OLE --> 0.91 XO_2 + FORM + 0.09 XO_2N + ALD2 + NO_2 - PAR	11.35	0

TABLE A-1. CB-4 MECHANISM (CONTINUED)

	Reaction	Rate Constant at 298°K (ppm^{-1} min^{-1})	Activation Energy (°K)
60.	O + ETH --> FORM + 1.7 HO_2 + CO + 0.7 XO_2 + 0.30 H	1080	792
61.	OH + ETH --> XO_2 + 1.56 FORM + 0.22 ALD2 + HO_2	1.192×10^4	- 411
62.	O_3 + ETH --> FORM + 0.42 CO + 0.13 HO_2	2.702×10^{-3}	2633
63.	TOL + OH --> 0.44 HO_2 + 0.8 XO_2 + 0.36 CRES + 0.56 TO_2	9150	- 322
64.	TO_2 + NO --> 0.9 NO_2 + 0.9 HO_2 + 0.9 OPEN	1.2×10^4	0
65.	TO_2 --> CRES + HO_2	250	0
66.	OH + CRES --> 0.4 CRO + 0.6 XO_2 + 0.6 HO_2 + 0.3 OPEN	6.1×10^4	0
67.	CRES + NO_3 --> CRO + HNO_3	3.25×10^4	0
68.	CRO + NO_2 -->	2×10^4	0
69.	OPEN --> C_2O_3 + HO_2 + CO	8.4	0
70.	OPEN + OH --> XO_2 + 2 CO + 2 HO_2 + C_2O_3 + FORM	4.4×10^4	0
71.	OPEN + O_3 --> 0.3 ALD2 + 0.62 C_2O_3 + 0.7 FORM + 0.3 XO_2 + 0.69 CO + 0.8 OH + 0.76 HO_2 + 0.2 MGLY	0.015	500
72.	OH + XYL --> 0.7 HO_2 + 0.5 XO_2 + 0.2 CRES + 0.8 MGLY + 1.1 PAR + 0.2 TO_2	3.62×10^4	- 116
73.	OH + MGLY --> XO_2 + C_2O_3	2.6×10^4	0
74.	MGLY --> C_2O_3 + HO_2 + CO	8.96	0

TABLE A-1. CB-4 MECHANISM (CONTINUED)

Reaction	Rate Constant at 298 °K (ppm^{-1} min^{-1})	Activation Energy (°K)
75. O + ISOP --> 0.6 HO_2 + 0.8 ALD2 + 0.55 OLE + 0.5 XO_2 + 0.5 CO + 0.45 ETH + 0.9 PAR	2.7×10^4	0
76. OH + ISOP --> XO_2 + FORM + 0.67 HO_2 + 0.13 XO_2N + ETH + 0.4 MGLY + 0.2 C_2O_3 + 0.2 ALD2	1.42×10^5	0
77. O_3 + ISOP --> FORM + 0.4 ALD2 + 0.55 ETH + 0.2 MGLY + 0.1 PAR + 0.06 CO + 0.44 HO_2 + 0.1 OH	.018	
78. NO_3 + ISOP --> XO_2 N	470	0
79. XO_2 + NO --> NO_2	1.2×10^4	0
80. XO_2N + NO -->	1000	0
81. XO_2 + XO_2 -->	2000	- 1300
82. NR --> NR	1	0

APPENDIX B

ESTIMATION OF MIXING HEIGHTS FOR USE IN OZIPM4

In OZIPM4, the rate of dilution of atmospheric pollutants is governed by the diurnal change in mixing height. The mixing height is the top of a surface-based layer of air which is well-mixed due to mechanical and thermal turbulence. As described in Section 3.2.2, the input variables required for OZIPM4 include: the mixing height at 0800 LCT, the maximum mixing height, the time at which the mixing height begins to rise if it starts to rise after 0800 LCT, and the time at which the mixing height reaches its maximum. The rate of rise is computed internally by OZIPM4.

Three different procedures exist for determining daily morning and afternoon mixing heights. The recommended procedure entails the use of temperature soundings taken routinely by the National Weather Service at various locations throughout the United States. If more direct measurements are available (e.g., radiosondes taken in the urban area or sodar data), they may be used instead of NWS data. If neither of the above two sets of measurements can be used, then the use of 250 m for the 0800 LCT mixing height and the climatological mean value for the maximum mixing height is recommended. The procedures to be followed for each approach are described below.

B.1 RECOMMENDED PROCEDURE USING NWS RADIOSONDES

Temperature soundings are taken by the NWS at sites throughout the United States. Soundings are usually taken every 12 hours at 1200 and 0000 Greenwich Mean Time (GMT), corresponding to 0800 and 2000 Eastern Daylight Time, respectively. Therefore, to estimate daily mixing heights (1), a NWS site must be selected which is representative of the city of interest,

(2) appropriate sounding data and urban surface data must be obtained, and (3) these data must be used to compute the morning and maximum mixing heights. Each of these steps is discussed below.

B.1.1 Site Selection

In selecting a NWS site as the basis for mixing height estimation, care should be taken to ensure that the site is meteorologically representative of the city of interest. Table B-1 contains recommended sites for a number of cities. Backup sites are listed for those cases in which radiosonde data may not be available for a given day, or if the site has significantly different meteorological conditions. Examples of the latter are the case in which a surface front lies between the sounding site and the city or the city is clear but cloudiness or precipitation occurs at the sounding site.

B.1.2 Selection of Day Specific Data

The daily morning mixing height for the model is normally estimated using the 1200 GMT (0800 EDT) sounding, while the maximum mixing height is estimated using the 0000 GMT (2000 EDT) sounding. In some cases, these soundings may not be available or appropriate and alternate approaches will be necessary. Table B-2 summarizes the order of preference in selecting the radiosondes for estimating the daily mixing heights. The actual data may be obtained from the National Climatic Center (NCC).*

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*National Climatic Center, Federal Building, Asheville, NC 28801
Telephone: (704) 258-2850, x203
Please allow about 4 weeks for NCC to fill an order.

TABLE B-1. NWS RADIOSONDE STATIONS

City	Primary	Backup(s)	Climatological Mixing Heights (m AGL) MAX
Allentown, PA	NYC, NY; Atl City, NJ	Albany, NY; Dullas AP, VA	1825
Baltimore, MD	Dulles AP, VA	Wallops Is., VA; Atl City, NJ	1825
Boston, MA	Portland, ME	Albany, NY; Chatham, MA	1375
Bridgeport, CT	NYC, NY; Atl City, NJ	Albany, NY	1500
Chicago, IL/IN	Peoria, IL	Green Bay, WI	1575
Cincinnati, OH/KY	Dayton, OH	Huntington, WV	1650
Cleveland, OH	Dayton, OH	Buffalo, NY	1650
Dayton, OH	*Dayton, OH	Huntington, WV	1661
Denver, CO	*Denver, CO	Grand Junction, CO	3358
Detroit, MI	Flint, MI	Dayton, OH	1700
Fresno, CA	Oakland, CA	Vandenberg AFB, CA	2000
Hartford, CT	Albany, NY	NYC, NY; Atl City, NJ	1500
Houston, tX	Victoria, TX	Lake Charles, LA	1525
Indianapolis, IN	Dayton, OH	Peoria, IL; Salem, IL	1600
Los Angeles, CA	Vandenberg AFB, CA	San Diego, CA	603
Louisville, KY/IN	Dayton, OH	Nashville, TN	1700
Milwaukee, WI	Green Bay, WI	Peoria, IL	1575
Nahsville, TN	*Nashville, TN	Jackson, AL	1845
New Haven, CT	NYC, NY; Atl City, NJ	Albany, NY	1450
New York, NY/NJ	*NYC, NY; Atl City, NJ	Albany, NY	1512
Philadelphia, PA/NJ	NYC, NY; Atl City, NJ	Dulles AP, VA	1700
Phoenix, AZ	Tucson, AZ	Winslow, AZ	3250
Pittsburg, PA	*Pittsburgh, PA	Dayton, OH; Dulles AP, A	1794
Portland, OR	Salem, OR	Medford, OR; Quilayute, WA	1575
Providence, RO	New York, NY	Albany, NY; Chatham, MA; Atl City, NJ	1350
Richmond, VA	Dulles AP, VA	Greensboro, NC; Wallops Is., VA	1725
Sacramento, CA	Oakland, CA	Vandenberg AFB, CA	1600
St. Louis, MO/IL	Salem, IL	Peoria, IL; Monette, MO	1625
Salt Lake City, UT	*Salt Lake City, NT	Grand Junction, CO	3673
San Bernardino, CA	San Diego, CA	Vandenberg AFB, CA .	1200
San Diego, CA	*San Diego, CA	Vandenberg AFB, CA	564
San Francisco, CA	Oakland, CA	Vandenberg AFB, CA	625
Scranton, PA	NYC, NY; Atl City, NJ	Albany, NY; Atl City, NJ Dulles AP, VA	1850
Seattle, WA	Quilayute, WA	Salem, OR	1398
Springfield, MA	Albany, NJ	NYC, NY; Atl City, NJ	1600
Trenton, NJ	NYC, NY; Atl City, NJ	Dulles AP, VA	1700

TABLE B-1 (CONTINUED)

City	Primary	Backup(s)	Climatological Mixing Heights (m AGL) MAX
entura-Oxnard, CA	Vandenberg AFB, CA	San Diego, CA	610
ashington, DC/MD/VA	*Dulles AP, VA	Wallops Is., VA	1884
ilmington, DE	Dulles AP, VA; Atl City, NJ	Wallops Is., VA; New York, NY	1700
orcester, MA	Albany, NY	Portland, ME; Chatham, MA	1500
oungstown, OH	Pittsburg, PA	Buffalo, NY; Dayton, OH	1700

This station should be used unless the data are missing for all the times listed n Table A-2. However, if a frontal passage occurs between the time of maximum zone and the time of the launch of the 0000 GMT sounding (normally about 2300 MT), the 1200 GMT sounding from that site should be used.

OTE: The NYC, NY radiosonde station was replaced by Atlantic City, NJ on September 2, 1980.

TABLE B-2. PREFERENTIAL ORDER OF DATA SELECTION

Morning Mixing Height Estimate

1. 1200 GMT Sounding at Primary Site
2. 0600 GMT Sounding at Primary Site*
3. 1200 GMT Sounding at Backup Site
4. 0600 GMT Sounding at Backup Site*

Maximum Mixing Height Estimate

1. 0000 GMT Sounding at Primary Site
2. 1800 GMT Sounding at Primary Site*
3. 1200 GMT Sounding at Primary Site
4. 0000 GMT Sounding at Backup Site
5. 1800 GMT Sounding at Backup Site*
6. 1200 GMT Sounding at Backup Site

---

*Soundings are not normally taken at these times, but may be available in some instances.

In addition to the sounding data, surface temperature and pressure data are also needed for each day modeled. The urban surface temperature at 0800 LCT (or the average temperature between 0800-0900 LCT) and the maximum temperature occurring prior to 1800 LCT are needed to estimate the morning and maximum mixing height, respectively. The surface temperature data should be measured to the nearest 0.1° C at a well ventilated site (EPA, 1986). The site should be located near the center of the urban area. Surface atmospheric pressure measurements are needed at the same time and location of the urban surface temperature measurements, if at all possible. If these measurements are not available, a local NWS or Federal Aviation Administration weather reporting station's barometer reading may be used.

If the elevation of the pressure reading and the urban temperature site are different, an adjustment should be made to the pressure measurement using equation (3)

$$P_{sfc} = P_{obs} + [.11\text{mb/m} \times (Z_{obs} - Z_{sfc})] \tag{3}$$

where

Z_{obs} = the elevation, in meters above sea level (mASL), of the pressure measurement

Z_{sfc} = the elevation (mASL) of the urban temperature measurement

P_{obs} = the pressure, in millibars, at Z_{obs}

P_{sfc} = the pressure, in millibars, at the urban temperature site

NOTE: Z_{obs} will be equal to zero meters ASL when a pressure reduced at sea level is used.

The value of P_{sfc} from equation (3) is an approximate value and can be rounded to the nearest whole millibar.

B.1.3 Mixing Height Estimation

The procedures for estimating the 0800 LCT mixing height and the maximum mixing height are outlined in Table B-3. The procedures in Table B-3 are designed for use with the worksheet displayed in Table B-4. Figure B-1 contains a flow diagram of the process. The procedures use the mandatory and significant pressure levels reported for each sounding (Table B-5). The steps lead to determination of the height at which the adiabatic lapse rate (extended from the surface temperature and pressure) intersects the vertical temperature profile). (For background information, the reader is referred to Wanta and Lowry, 1976; Hewson, 1976; and Slade, 1968). An example problem is presented in Section B.4.

In some instances, the mixing heights estimated by this procedure may not be representative. If the 0800 LCT morning mixing height is estimated to be less than 250 meters, then a value of 250 meters should be used. This assumed minimum value for the 0800 LCT mixing height accounts for the effects of mixing due to mechanical turbulence caused by increased surface roughness in the urban area (Godowitch, et al, 1979; and Bentley and Schulman, 1979). Similarly, if the city's maximum mixing height is greater than twice the climatological maximum value (e.g., see Table B-1), the surface temperature and pressure used and the choice of sounding site should be checked for representativeness using the guidelines in B.1.1 and B.1.2 above. If no backup data are available, twice the climatological value should be used as the maximum. Also, a maximum mixing height less than or equal to the morning

TABLE B-3. PROCEDURES FOR ESTIMATING MIXING HEIGHTS

Step 1 -- For reference, the information at the top of Table B-4 should be listed (e.g., date, city, etc.). If the morning mixing height is to be calculated, the 0800 LCT surface data are used. If the maximum mixing height is to be calculated, the data corresponding to the time of maximum temperature (i.e., between 800-1800 LCT) are used. In the row labled URBAN SURFACE DATA, enter the following information: (1) the elevation of the urban temperature site in meters above sea level; (2) the surface pressure in millibars (this value is P_{sfc}); and (3) the surface temperature in degrees Celsius (°C).

Convert the surface temperature in column four to degrees Kelvin (°K) by adding 273.2, and enter the result in column five. This value is T_{sfc}(°K).

Use Equation 1 below and the values just entered to calculate the potential temperature at the surface (0$_{sfc}$ in °K to the nearest 0.1°K) and enter this value under column six "(°K)."

$$_{sfc}\ (\text{in }^\circ\text{K}) = T_{sfc}\ (\text{in }^\circ\text{K})\ {\frac{P_{sfc}\ (\text{in mb})}{1000\ \text{mb}}}^{-0.286} \qquad (1)$$

Step 2 -- Using the temperature sounding data, find the highest pressure level other than the sounding's surface value that is less than the pressure at the urban surface.[**] From this pressure level on the sounding, enter the height (if listed), pressure, and temperature (in °C) into the row marked "(2)" on Table B-4.

[**] For example, if the urban surface pressure is 985 mb, and the sounding pressures are: 1005, 1000, 963, 850 mb, etc., 963 mb is the "highest pressure level that is less than the pressure at the urban surface." 850 mb is the "next lowest pressure level" needed in Step 4.

TABLE B-3 (CONTINUED)

Step 3 -- Convert the temperature at this level to the Kelvin scale and enter in column 5. Compute the potential temperature ($_p$) to the nearest 0.1°K using the pressure (P, in mb) and temperature (T_p in °K) at this level in Equation 2 below:

$$_p \text{ (in °K)} = T_p \text{ (in °K)} \ \frac{P \text{ (in mb)}}{1000 \text{ mb}}^{-0.286} \qquad (2)$$

Enter the value of $_p$ found from Equation (2) into the same row under the column labeled "(K)$_p$."

Step 4 -- If the potential temperature of the last row that was entered is greater than the potential temperature $_{sfc}$, and this is the first level above the surface, then 250 meters should be used as the mixing height (if given), pressure and temperature of the next lowest pressure level found on the sounding into the next row of Table B-4 and return to Step 3.

Step 5 -- The mixing height is between the last two levels entered into Table B-4. If height values are given for both of these levels, the elevation of the mixing height can be found using Step 6. If one of the levels does not have a height value, use linear interpolation to find the pressure value for the potential temperature value $_{sfc}$ + 0.1°K. Enter this pressure into the row marked "MIXING HEIGHT" at the bottom of Table B-4 under the column "PRESSURE in mb." Proceed to Step 7.

Step 6 -- From the two levels where height is given on the sounding surrounding the mixing height level, use linear interpolation to find the height (in meters ASL) at the value $_{sfc}$ + 0.1°K (i.e., the potential temperature at the mixing height). Enter the value found by linear interpolation into the row labeled "MIXING HEIGHT" under the column "HEIGHT (mASL)" and proceed to Step 8.

Step 7 -- Use linear interpolation to find the height above sea level of the mixing height using the pressure at the mixing height (found in Step 5) and the pressure levels on the sounding above and below the mixing height pressure that have both pressure and height values. Enter the height value found into the row "MIXING HEIGHT" under the column marked "HEIGHT, (mASL)" and proceed to Step 8.

Step 8 -- Subtract the elevation of the urban site (mASL) from the height (mASL) of the mixing height. the result is the height of the mixing height in meters above the surface of the city (mAGL). Enter this value into Table B-4.

NOTE: Despite the fact that pressure and height, and potential temperature and height, are not linearly related, linear interpolation does not produce significant errors over the limited ranges used above.

TABLE B-4. WORKSHEET FOR COMPUTING MIXING HEIGHTS

Date:
Time of Mixing Height for Input Into Model:
City:
Sounding Method:
Time of Sounding:
LCT. Surface Elevation: mASL
Location of Sounding:

LOCATION OF URBAN SURFACE AREA (IF DIFFERENT THAN ABOVE)

1	2	3	4	5	6	7
LEVEL	HEIGHT (mASL)	PRESSURE (mb)	TEMP. (°C)	TEMP. (°K)	(°K)	REMARKS
Urban Surface Data (1)						<--sfc
(2)						

	0_{sfc} + 0.1°K (°K)	PRESSURE (mb)	HEIGHT (mASL)	Height (mAGL)	HEIGHT USED IN MODEL (mAGL)
MIXING HEIGHT					

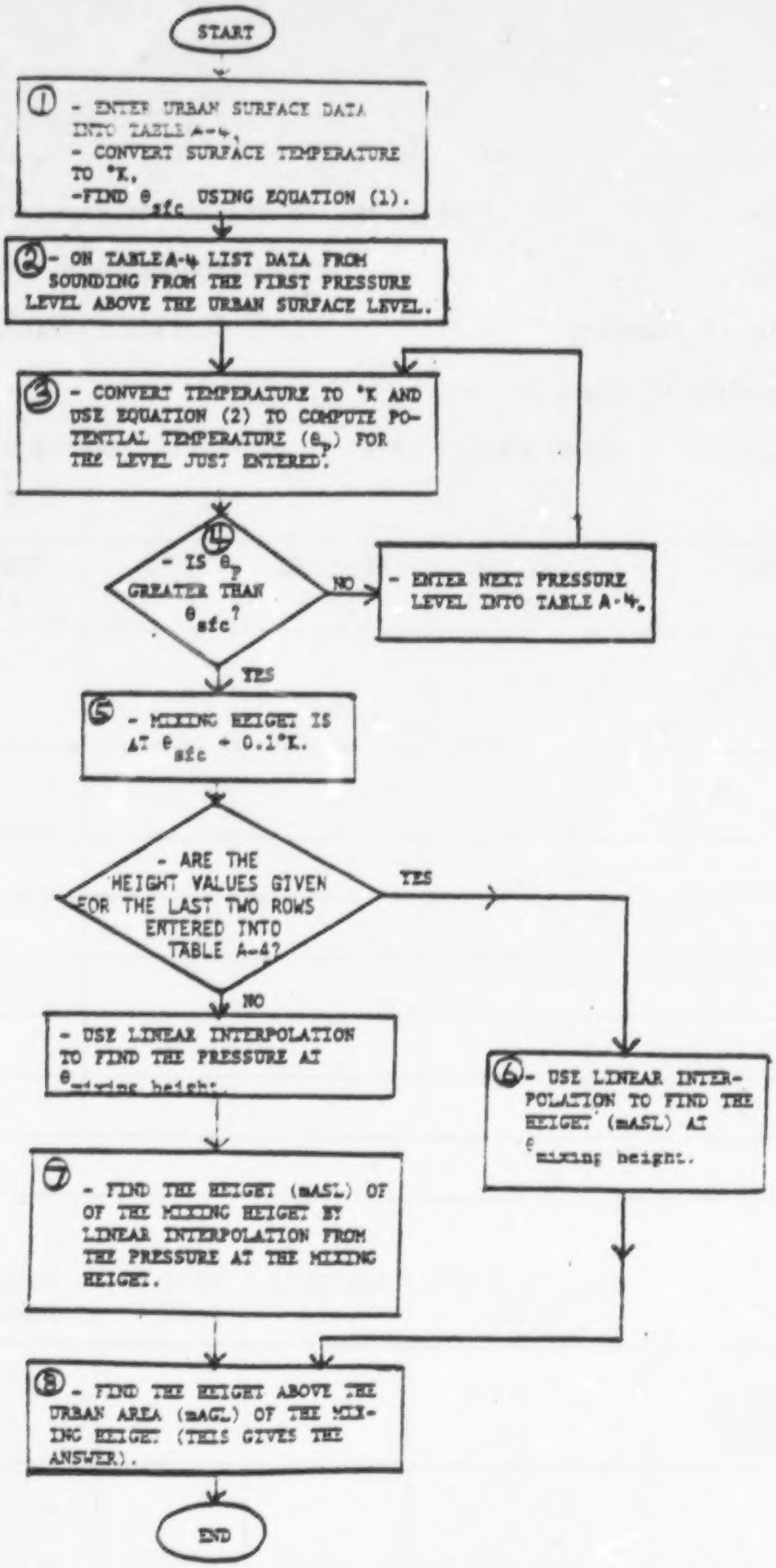
START
① - ENTER URBAN SURFACE DATA INTO TABLE A-4.
- CONVERT SURFACE TEMPERATURE TO °K.
-FIND θ_{sfc} USING EQUATION (1).
② - ON TABLE A-4 LIST DATA FROM SOUNDING FROM THE FIRST PRESSURE LEVEL ABOVE THE URBAN SURFACE LEVEL.
③ - CONVERT TEMPERATURE TO °K AND USE EQUATION (2) TO COMPUTE POTENTIAL TEMPERATURE (θ_p) FOR THE LEVEL JUST ENTERED.
④ - IS θ_p GREATER THAN θ_{sfc}?
NO
- ENTER NEXT PRESSURE LEVEL INTO TABLE A-4.
YES
⑤ - MIXING HEIGHT IS AT θ_{sfc} + 0.1°K.
- ARE THE HEIGHT VALUES GIVEN FOR THE LAST TWO ROWS ENTERED INTO TABLE A-4?
YES
NO
- USE LINEAR INTERPOLATION TO FIND THE PRESSURE AT $\theta_{mixing\ height}$.
⑥ - USE LINEAR INTERPOLATION TO FIND THE HEIGHT (mASL) AT $\theta_{mixing\ height}$.
⑦ - FIND THE HEIGHT (mASL) OF OF THE MIXING HEIGHT BY LINEAR INTERPOLATION FROM THE PRESSURE AT THE MIXING HEIGHT.
⑧ - FIND THE HEIGHT ABOVE THE URBAN AREA (mAGL) OF THE MIXING HEIGHT (THIS GIVES THE ANSWER).
END

Figure B-1. Flow Chart for Table B-3. Numbers in circles are step numbers in Table B-3.

TABLE B-5. SURFACE AND SOUNDING DATA

Hour Starting at. LCT	Temperature °C	Pressure, mb
8	23.2	1010.3
9	23.9	1010.7
10	25.8	1010.8
11	27.3	1010.6
12	28.7	1010.3
13	29.3	1010.0
14	30.1	1009.6
15	30.4	1009.2
16	30.8	1008.8
17	31.4	1008.6
18	31.2	1008.5

Sounding Data

1200 GMT Sounding

Pressure (mb)	Height (m ASL)	Temp. (°C)
S 1015	8*	23.0
M 1000	139	23.0
S 967	---	24.4
M 850	1550	16.2
S 827	---	14.2
S 817	---	13.6
M 700	3168	4.6
S 680	---	5.6
S 661	---	5.6
S 608	---	0.4
M 500	5860	- 8.3
S 491	---	- 9.3
S 453	---	-12.7
S 438	---	-13.9
M 400	7560	-18.7
S 388	---	-20.1
S 349	---	-26.3
S 324	---	-29.7
M 300	9640	-33.7
S 267	---	-39.5
M 250	10890	-47.7
M 200	12370	-51.7
M 150	14190	-60.9
S 148	---	-61.5

0000 GMT Sounding

Pressure (mb)	Height (m ASL)	Temp (°C)
S 1012	8*	31.0
M 1000	114	30.6
M 850	1537	16.4
S 831	---	15.4
S 791	---	13.2
S 778	---	11.8
S 760	---	11.2
M 700	3164	7.0
S 628	---	1.6
S 560	---	- 1.5
M 500	5860	- 7.3
M 400	7560	-18.9
S 371	---	-21.7
M 300	9650	-33.1
S 265	---	-39.9
M 250	10900	-42.9
S 205	---	-52.9
M 200	12370	-53.3
M 150	14190	-61.1
S 127	---	-64.9
S 120	---	-61.7
M 100	16690	-63.3
M 70	18900	-58.5
M 50	21040	-54.5
M 30	24350	-49.9
M 20	27030	-44.7
S 15	---	-42.1

NOTE: M = Mandatory Levels and S = Significant Levels
If NWS data are used, both the mandatory and significant levels are needed.
The 0000 GMT sounding is the following day in GMT.
*The lowest level of the sounding should not be used in the mixing height calculations.

mixing height, or less than one-third the climatological maximum mixing height value is suspect. Using data from a backup site may provide a more realistic value. However, if the low afternoon mixing height is due to the existence of a surfacebased stable layer, an adjustment to the procedures outlined in Table B-3 can be employed. Replace the "Urban Surface Data" with the following data from the sounding site: (1) the maximum temperature, (2) the estimated or observed surface pressure at the time of maximum temperature, and (3) the height of the sounding surface level. Then compute the mixing height according to the procedure in Table B-3. If this problem occurs on a majority of modeling days, then an alternative, more representative site should be used for all the modeling days.

B.2 USE OF ALTERNATE DATA

Other, more direct measurements of mixing height may be used to increase the representativeness of the estimated values. These methods include direct urban temperature sounding and sodar data. The measurements should be taken over the urban area near the center of the city at 0800 LCT, and close to the time of the climatological maximum surface temperature. It is not recommended that these measurements be taken specifically for the OZIPM4/EKMA techniques; however, they may be employed if available. Examples are discussed below.

1. Local Urban Radiosonde -- The methods described in Section B.1.3 can be used to find the mixing height from radiosondes taken within the urban area as opposed to NWS sites. The radiosonde surface temperature and pressure should be used in place of the URBAN SURFACE DATA.

2. Urban Helicopter Soundings -- Similarly, vertical temperature profiles obtained from helicopter soundings can be used in place of the NWS soundings. The urban site surface temperature and pressure should be used as the URBAN SURFACE DATA.

3. Sodar -- (also known as Acoustic Radar) the mixing height found by sodar (in mAGL) can be used directly in the model.

NOTE: Regardless of the procedure applied, the limitations concerning the morning and maximum mixing heights that were described in Section B.1.3 should be observed.

B.3 USE OF CLIMATOLOGICAL MEANS

If radiosonde data are not available, 250 m should be used for the 0800 LCT mixing height and the city-specific climatological mean value may be used for the maximum mixing height. Table B-1 lists representative values for several cities, and Holzworth, 1972, contains information for the contiguous United States. If Holzworth is used, values for summer, nonprecipitation days should be used. The appropriate starting and ending tiems of the mixing height rise in the model are 0800 LCT and the time of the maximum temperature. If the latter is unknown, 1400 LST (1500 LDT) may be assumed.

B.4 EXAMPLE PROBLEM

To illustrate the procedure described in Section B.1.3, an example problem is included for reference. Table B-5 shows relevant data typically available. Note that both the 1200 GMT and the 0000 GMT soundings are used in the calculations, the former for the morning mixing height and the latter for the maximum mixing height. Table B-6 shows the individual computational steps for the morning mixing height calculation, while Table B-7 shows the same for the maximum mixing height.

TABLE B-6. MORNING MIXING HEIGHT DETERMINATION

Example from Table B-5:

08 LCT temperature = 23.2°C
Maximum temperature after 08 LCT = 3.4°C at 17 LCT
08 LCT pressure = 1010.3 mb
Pressure at time of maximum temperature (1700 LCT) = 1008.6 mb Time of morning mixing height = 0800 LCT
Time of maximum mixing height = 1700 LCT

Problem:

Find the 0800 LCT mixing height using data from the sounding shown in Table B-5 (i.e., the 1200 GMT sounding). A worksheet is shown as Table B-6A. The elevation of the urban surface site is 62 mASL.

Solution:

STEP 1

Enter 62., 1010.3, and 23.2 into row (1) of Table B-6A
(URBAN SURFACE DATA)
Temp (°C) = 23.2
Converted to °K = 23.2 + 273.2 = 296.4°K
Enter 296.4 into row (1) of Table B-6A under "TEMP(°K)" Using Equation (1) on the Urban Surface Data:

$$0_{sfc} = 296.4^{\circ}\text{K} \left[\frac{1010.3 \text{ mb}}{1000 \text{ mb}} \right]^{-0.286}$$

$$0_{sfc} = 295.5^{\circ}\text{K}$$

STEP 2 - Enter 139., 1000., and 23.0 into row (2) of Table B-6A

STEP 3 - 23.0 + 273.2 = 296.2°K

Using Equation (2):

$$0_p = 296.2^\circ\text{K} \left[\frac{1000 \text{ mb}}{1000 \text{ mb}} \right]^{-0.286}$$

0_p = 296.2°K (enter this value into Table B-6A)

STEP 4 - 0_p (296.2°K) is greater than 0_{sfc} (295.5°K).

Since 0_p is from the first level above the surface, the 250 m default value should be used for the 0800 LCT mixing height.

TABLE B-6A. EXAMPLE (HYPOTHETICAL DATA)

Date: Date of Modeling Time of Mixing Height for Input Into Model: 0800 EDT

City: City to be Modeled Sounding Method: NWS, Urban Radiosonde or Helicopter

Time of Sounding: 0800 LCT. Surface Elevation: (of sounding) mASL

Location of Sounding: Name of Sounding Site

LOCATION OF URBAN SURFACE DATE (IF DIFFERENT THAN ABOVE) - Street Address, Building or Park, etc.

1	2	3	4	5	6	7
LEVEL	HEIGHT (mASL)	PRESSURE (mb)	TEMP. (°C)	TEMP. (°K)	(°K)	REMARKS
Urban Surface Data (1)	62	1010.3	23.2	296.4	295.5	<--sfc
(2)	139	1000.	23.0	296.2	296.2	level is higher than sfc + 0.1 °K

	0_{sfc} + 0.1°K (°K)	PRESSURE (mb)	HEIGHT (mASL)	Height (mAGL)	HEIGHT USED IN MODEL (mAGL)
MIXING HEIGHT	295.6	---	0	0	250

TABLE B-7. MAXIMUM MIXING HEIGHT DETERMINATION

Example from Table B-5:

08 LCT temperature = 23.2°C
Maximum temperature = 31.4°C at 17 LCT
08 LCT pressure = 1010.3 mb
17 LCT pressure = 1008.6 mb
Time of morning mixing height = 0800 LCT
Time of maximum mixing height = 1700 LCT

Problem:

Find the maximum afternoon mixing height using data from the sounding shown in Table B-5 (i.e., the 0000 GMT sounding). A worksheet is shown as Table B-7A. The elevation of the urban site is 62 mASL.

Solution:

STEP 1

Enter 62, 1008.6, and 31.4 into row (1) of Table B-7A (Urban Surface Data)

Temp (°C) = 31.4°C
Converted to °K = 31.4 + 273.2 = 304.6°K
Enter 304.6°K into row (1) of Table B-7A under "Temp (°K)"
Using Equation (1) on the Urban Surface Data

$$_{\text{sfc}} = 304.6^{\circ}\text{K} \left[\frac{1000 \text{ mb}}{1000 \text{ mb}} \right]^{-0.286}$$

$$_{\text{sfc}} = 303.9$$

STEP 2

Enter 114., 1000., and 30.6 into Table B-7A.

TABLE B-7 (CONTINUED)

STEP 3

$30.6^{\circ}C + 273.2 = 303.8^{\circ}K$

Using Equation (2):

$${}_p = 303.8^{\circ}K \left[\frac{1000 \text{ mb}}{1000 \text{ mb}}\right]^{-0.286}$$

$${}_p = 303.4^{\circ}K$$

STEP 4 - 303.8°K is less than 303.9°K

Therefore, enter 1537., 850., and 16.4 in Table B-7A and return to STEP 3.

STEP 3 - $16.4^{\circ}C = 273.2 = 289.6^{\circ}K$

Using Equation (2)

$${}_p = 289.6^{\circ}K \left[\frac{850 \text{ mb}}{1000 \text{ mb}}\right]^{-0.286}$$

$${}_p = 303.4^{\circ}K$$

STEP 4 - 303.4°K is less than 303.9°K

Therefore, enter 831. and 15.4 into Table B-7A (note that there is no height value for this pressure level) and return to STEP 3.

STEP 3 - $15.4^{\circ}C = 273.2 = 288.6^{\circ}K$

Using Equation (2):

$${}_p = 296.2^{\circ}K \left[\frac{831 \text{ mb}}{1000 \text{ mb}}\right]^{-0.286}$$

$${}_p = 304.3^{\circ}K$$

TABLE B-7 (CONTINUED)

STEP 4 - 304.3°K is greater than 303.9°K

STEP 5

$$_{\text{sfc}} + 0.1^\circ\text{K} = 303.9^\circ\text{K} = 0.1^\circ\text{K} = 304.0^\circ\text{K}$$

Using linear interpolation from temperature (0) to pressure since a highest value is not given for the 831 mb pressure level

0 (°K)	Pressure (mb)
303.4	850
304.0	P mixing height
304.3	831

$$P_{\text{mixing height}} = 831\text{ mb} - \frac{(850\text{ mb} - 831\text{ mb})(304.0^\circ\text{K} - 304.3^\circ\text{K})}{304.3^\circ\text{K} - 303.4^\circ\text{K}}$$

$$= 831 - \frac{(19\text{ mb})(-0.3^\circ\text{K})}{0.9^\circ\text{K}}$$

$$= 837.3\text{ mb}$$

The pressure at the mixing height (rounded to the nearest whole millibar) is 837 mb.

STEP 7

Use linear interpolation to find the height above sea level of the mixing height. Enter 3164. and 700. into Table B-7A.

Pressure (mb)	Height (mASL)
850	1537.
837	Z mixing height
700	3164.

$$Z\text{ mixing height} = 1537\text{ m} + \frac{(3164\text{ m} - 1537\text{ m})(837\text{ mb} - 850\text{ mb})}{700\text{ mb} - 850\text{ mb}}$$

$$= 1537\text{ m} + \frac{(1627\text{ m})(-13\text{ mb})}{-150\text{ mb}}$$

$$Z\text{ mixing height} = 1678\text{ m}$$

TABLE B-7 (CONTINUED)

STEP 8

1678 mASL - height of mixing height
-62 mASL - elevation of urban surface site
1616 mAGL = mixing height in meters above the urban area

1616 m is the height of the maximum mixing height to be used in the model with the time of 1700 LCT

TABLE B-7A EXAMPLE (HYPOTHETICAL DATA)

Date: Time of Mixing Height for Input Into Model: 1700 EDT

City: Sounding Method: NWS

Time of Sounding: LCT. Surface Elevation: 3. mASL

Location of Sounding: Name of Sounding Site

LOCATION OF URBAN SURFACE AREA (IF DIFFERENT THAN ABOVE)

1	2	3	4	5	6	7
LEVEL	HEIGHT (mASL)	PRESSURE (mb)	TEMP. (°C)	TEMP. (°K)	(°K)	REMARKS
Urban Surface Data (1)	62	1008.6	31.4	304.6	303.9	<--sfc
(2)	114	1000.	30.6	303.8	303.8	Mixing height is between these two levels at ≈ 304.0°K
	1537	850.	16.4	289.6	303.4	
	---	831.	15.4	288.6	304.3	
	3164	700	---	---	---	Needed to provide upper height value for interpolation

	0_{sfc} + 0.1°K (°K)	PRESSURE (mb)	HEIGHT (mASL)	Height (mAGL)	HEIGHT USED IN MODEL (mAGL)
MIXING HEIGHT	304.0	837.	1678.	1616.	1616.

APPENDIX C

COMPUTATION OF CARBON BOND FRACTIONS FROM GC DATA

In this appendix, the computation of carbon-fractions from results of gas chromatographic (GC) analysis is discussed. As noted earlier, GC analysis actually measures the concentrations of individual organic species, which must then be grouped according to the CB-4 organic reactivity classes. In order to keep the computations relatively simple for illustrative purposes, hypothetical examples are discussed. For more detailed discussion, the reader is referred to EPA, 1989.

At the heart of the computational procedure is the definition of how individual species should be categorized according to carbon bond type. Definitions for numerous individual species and are listed in Table C-1. These definitions, or species profiles, give the number of bond types found in each CB-4 category. Using this information, along with the carbon numbers shown in Table 2-1, it is possible to compute concentrations of individual carbon bond classes, and then determine percentages of carbon in each class. These computations will be illustrated by the examples in Tables C-2 and C-3, respectively.

Table C-2 presents example calculations for a hypothetical example. The individual species that might be detected by GC analysis are shown in the left hand column, and their associated concentrations, in units of ppbC and ppb, are shown in the next two columns. The remaining columns are associated with the carbon bond computations.

TABLE C-1 SPECIES PROFILES BY BOND GROUPS FOR CB-4

COMPOUND NAME	PAR	OLE	ETH	TOL	XYL	FORM	ALD2	ISOP	NR
1,1,1-TRICHLOROETHANE									2.0
1,1,2-TRICHLOROETHANE									2.0
1,2,3,4-TETRAMETHYLBENZENE	2.0				1.0				
1,2,3,5-TETRAMETHYLBENZENE	2.0				1.0				
1,2,3-TRIMETHYLBENZENE	1.0				1.0				
1,2,4,5-TETRAMETHYLBENZENE	2.0				1.0				
1,2,4-TRIMETHYLBENZENE	1.0				1.0				
1,2-DIETHYLBENZENE	2.0				1.0				
1,2-DIMETHYL-3-ETHYLBENZENE	2.0				1.0				
1,2-DIMETHYL-4-ETHYLBENZENE	2.0				1.0				
1,3,5-TRIMETHYLBENZENE	1.0				1.0				
1,3-BUTADIENE		2.0							
1,3-DIETHYLBENZENE	2.0				1.0				
1,4-BUTANEDIOL	4.0								
1,4-DIETHYLBENZENE	2.0				1.0				
1-BUTENE	2.0	1.0							
1-BUTYNE	3.0								1.0
1-CHLOROBUTANE	4.0								
1-DECENE	8.0	1.0							
1-ETHOXY-2-PROPANOL	3.0						1.0		
1-HEPTENE	5.0	1.0							
1-HEXENE	4.0	1.0							
1-METHYLCYCLOHEXENE	5.0	1.0							
1-METHYL-2-ETHYLBENZENE	1.0				1.0				
1-METHYL-3-ETHYLBENZENE	1.0				1.0				
1-METHYL-3-ISOPROPYLBENZENE	2.0				1.0				
1-METHYL-3-N-PROPYLBENZENE	2.0				1.0				
1-METHYL-4-ISOPROPYLBENZENE	2.0				1.0				
1-NONENE	7.0	1.0							
1-OCTENE	6.0	1.0							
1-PENTENE	3.0	1.0							
1-UNDECENE	9.0	1.0							
2,2,3-TRIMETHYLBUTANE	7.0								
2,2,3-TRIMETHYLPENTANE	8.0								
2,2,4-TRIMETHYLPENTANE	8.0								
2,2,5-TRIMETHYLHEXANE	9.0								
2,2-DICHLORONITROANILINE	1.0								5.0
2,2-DIMETHYLBUTANE	6.0								
2,2-DIMETHYLHEXANE	8.0								
2,2-DIMETHYLPROPANE	5.0								
2,3,3-TRIMETHYLPENTANE	8.0								
2,3,3-TRIMETHYL-1-BUTENE	6.0					1.0			
2,3,4-TRIMETHYLPENTANE	8.0								
2,3,5-TRIMETHYLHEXANE	9.0								
2,3-DIMETHYLBUTANE	6.0								
2,3-DIMETHYLHEPTANE	9.0								
2,3-DIMETHYLHEXANE	8.0								
2,3-DIMETHYLOCTANE	10.0								
2,3-DIMETHYLPENTANE	7.0								
2,3-DIMETHYL-1-BUTENE	5.0					1.0			
2,4,4-TRIMETHYL-1-PENTENE	7.0					1.0			
2,4,5-TRIMETHYLHEPTANE	10.0								
2,4-DIMETHYLHEPTANE	9.0								
2,4-DIMETHYLHEXANE	8.0								

COMPOUND NAME	PAR	OLE	ETH	TOL	XYL	FORM	ALD2	ISOP	NR
2,4-DIMETHYLOCTANE	10.0								
2,4-DIMETHYLPENTANE	7.0								
2,5-DIMETHYLHEPTANE	9.0								
2,5-DIMETHYLHEXANE	8.0								
2,6-DIMETHYLOCTANE	10.0								
2,6-DIMETHYLSTYRENE		1.0			1.0				
2-BUTYLTETRAHYDROFURAN	6.0						1.0		
2-BUTYNE	3.0								1.0
2-ETHYLHEXANOL	8.0								
2-ETHYL-1-BUTENE	5.0					1.0			
2-ETHYL-1-HEXANOL	8.0								
2-FURFURAL	1.0	1.0					1.0		
2-HEXENE	2.0						2.0		
2-METHYLDECANE	11.0								
2-METHYLHEPTANE	8.0								
2-METHYLHEXANE	7.0								
2-METHYLOCTANE	9.0								
2-METHYLPENTANE	6.0								
2-METHYLPROPANE	4.0								
2-METHYLPROPENE	2.0	1.0							
2-METHYLPROPENE	2.0	1.0							
2-METHYL-1,3-BUTADIENE								1.0	
2-METHYL-1-BUTENE	4.0					1.0			
2-METHYL-1-PENTENE	5.0					1.0			
2-METHYL-2-BUTENE	3.0	1.0							
2-METHYL-2-PENTENE	4.0	1.0							
2-METHYL-3-HEXANONE	7.0								
2-(2-BUTOXYETHOXY)-ETHANOL	4.0						2.0		
3,3-DIMETHYLPENTANE	7.0								
3,4-DIMETHYLOCTANE	10.0								
3,5,5-TRIMETHYLHEXANE	9.0								
3,5-DIMETHYLHEPTANE	9.0								
3-HEPTENE	3.0						2.0		
3-METHYLHEPTANE	8.0								
3-METHYLHEXANE	7.0								
3-METHYLOCTANE	9.0								
3-METHYLPENTANE	6.0								
3-METHYL-1-BUTENE	3.0	1.0							
3-METHYL-1-PENTENE	4.0	1.0							
3-METHYL-CIS-2-PENTENE	4.0	1.0							
3-METHYL-TRANS-2-PENTENE	4.0	1.0							
3-(CHLOROMETHYL)-HEPTANE	8.0								
4,4-METHYLENE DIANILINE	1.0			1.0					5.0
4-METHYLANILINE				1.0					
4-METHYLHEPTANE	8.0								
4-METHYLNONANE	10.0								
4-METHYLOCTANE	9.0								
4-METHYL-1-PENTENE	4.0	1.0							
4-METHYL-CIS-2-PENTENE	2.0						2.0		
4-METHYL-TRANS-2-PENTENE	2.0						2.0		
4-PHENYL-1-BUTENE	1.0	1.0		1.0					
ACENAPHTHENE	1.0				1.0				3.0
ACENAPHTHYLENE		1.0			1.0				2.0
ACETALDEHYDE							1.0		

COMPOUND NAME	PAR	OLE	ETH	TOL	XYL	FORM	ALD2	ISOP	NR
ACETIC ACID	1.0								1.0
ACETIC ANHYDRIDE	2.0								2.0
ACETONE	3.0								
ACETYLENE	1.0								1.0
ACROLEIN (PROPENAL)		1.0				1.0			
ACRYLIC ACID		1.0							1.0
ACRYLONITRILE	1.0	1.0							
ADIPIC ACID	4.0								2.0
ALIPHATICS (per carbon)	1.0								
ALKENE KETONE	2.0	1.0							
AMINOANTHRAQUINONE	2.0								12.0
ANILINE	1.0								5.0
ANTHANTHRENE		1.0		1.0	1.0				7.0
ANTHRACENE	1.0				1.0				5.0
ANTHRAQUINONE	2.0								12.0
A-PINENE	6.0	0.5					1.5		
BENZALDEHYDE							1.0		5.0
BENZENE	1.0								5.0
BENZOIC ACID	1.0								6.0
BENZOPYRENES		1.0		1.0	1.0				3.0
BENZOTHIAZOLE	2.0								5.0
BENZO(a)ANTHRACENE				1.0	1.0				3.0
BENZO(a)PYRENE		1.0		1.0	1.0				3.0
BENZO(b)FLUORANTHENE				1.0	1.0				5.0
BENZO(c)PHENANTHRENE				1.0	1.0				3.0
BENZO(e)PYRENE		1.0		1.0	1.0				3.0
BENZO(g,h,i)FLUORANTHENE				1.0	1.0				3.0
BENZO(g,h,i)PERYLENE	1.0			1.0	1.0				6.0
BENZO(k)FLUORANTHENE				1.0	1.0				5.0
BENZYLCHLORIDE				1.0					
BIPHENYL				1.0					5.0
BIPHENYLOL				1.0					5.0
BROMODINITROANILINE	1.0								5.0
BROMODINITROBENZENE	1.0								5.0
BUTENE	2.0	1.0							
BUTOXYBUTENE	4.0	1.0					1.0		
BUTOXYETHOXYETHANOL	4.0						2.0		
BUTOXYETHOXYETHANOL ACETATE	5.0						2.0		1.0
BUTYL CARBITOL	4.0						2.0		
BUTYL CELLOSOLVE	4.0						1.0		
BUTYLACRYLATE	4.0	1.0							1.0
BUTYLBENZENE	3.0			1.0					
BUTYLBENZOATE	5.0								6.0
BUTYLBENZYLPHTHALATE	5.0			1.0					7.0
BUTYLCYCLOHEXANE	10.0								
BUTYLISOPROPYLPHTHALATE	8.0								7.0
BUTYRALDEHYDE	2.0						1.0		
B-PHELLANDRENE	6.0	2.0							
B-PINENE	8.0	1.0							
C1 COMPOUNDS (DIESEL EXHAUST)	0.01								0.99
C10 AROMATIC	3.0			1.0					
C10 COMPOUNDS (DIESEL EXHAUST)	5.48	0.189		0.289	0.265				
C10 OLEFINS	8.0	1.0							
C10 PARAFFINS	10.0								

COMPOUND NAME	PAR	OLE	ETH	TOL	XYL	FORM	ALD2	ISOP	NR
C10H12	2.0				1.0				
C10H1[illegible]	10.0								
C10H160	8.0	1.0							
C11 COMPOUNDS (DIESEL EXHAUST)	10.7	0.15							
C11 OLEFINS	9.0	1.0							
C11 PARAFFIN	11.0								
C11H10	3.0				1.0				
C11H140	2.0				1.0				1.0
C12 COMPOUNDS (DIESEL EXHAUST)	5.0			1.0					
C12 OLEFINS	10.0	1.0							
C12 PARAFFIN	12.0								
C12H22	12.0								
C13 COMPOUNDS (DIESEL EXHAUST)	6.0			1.0					
C13 PARAFFIN	13.0								
C14 COMPOUNDS (DIESEL EXHAUST)	7.0			1.0					
C15 COMPOUNDS (DIESEL EXHAUST)	8.0			1.0					
C16 BRANCHED ALKANE	16.0								
C16 COMPOUNDS (DIESEL EXHAUST)	9.0			1.0					
C17 COMPOUNDS (DIESEL EXHAUST)	10.0			1.0					
C18 COMPOUNDS (DIESEL EXHAUST)	11.0			1.0					
C19 COMPOUNDS (DIESEL EXHAUST)	12.0			1.0					
C2 ALKYLANTHRACENES	3.0				1.0				5.0
C2 ALKYLBENZANTHRACENE	2.0			1.0	1.0				3.0
C2 ALKYLBENZOPHENANTHRENE	2.0			1.0	1.0				3.0
C2 ALKYLCHRYSENES	2.0			1.0	1.0				3.0
C2 ALKYLCYCLOHEXANE	8.0								
C2 ALKYLINDAN	3.0				1.0				
C2 ALKYLNAPTHALENE	4.0				1.0				
C2 ALKYLPHENANTHRENES	3.0				1.0				5.0
C2 COMPOUNDS (DIESEL EXHAUST)	0.77		0.115						1.0
C20 COMPOUNDS (DIESEL EXHAUST)	13.0			1.0					
C21 COMPOUNDS (DIESEL EXHAUST)	14.0			1.0					
C22 COMPOUNDS (DIESEL EXHAUST)	15.0			1.0					
C23 COMPOUNDS (DIESEL EXHAUST)	16.0			1.0					
C24 COMPOUNDS (DIESEL EXHAUST)	17.0			1.0					
C25 COMPOUNDS (DIESEL EXHAUST)	18.0			1.0					
C26 COMPOUNDS (DIESEL EXHAUST)	19.0			1.0					
C27 COMPOUNDS (DIESEL EXHAUST)	20.0			1.0					
C28 COMPOUNDS (DIESEL EXHAUST)	21.0			1.0					
C29 COMPOUNDS (DIESEL EXHAUST)	22.0			1.0					
C3 ALKYLCYCLOHEXANE	9.0								
C3 ALKYLSTYRENE	2.0	1.0		1.0					
C3 COMPOUNDS (DIESEL EXHAUST)	1.07	0.904							0.122
C3 PARAFFIN	3.0								
C30 COMPOUNDS (DIESEL EXHAUST)	23.0			1.0					
C31 COMPOUNDS (DIESEL EXHAUST)	24.0			1.0					
C32 COMPOUNDS (DIESEL EXHAUST)	25.0			1.0					
C33 COMPOUNDS (DIESEL EXHAUST)	26.0			1.0					
C34 COMPOUNDS (DIESEL EXHAUST)	27.0			1.0					
C35 COMPOUNDS (DIESEL EXHAUST)	28.0			1.0					
C36 COMPOUNDS (DIESEL EXHAUST)	29.0			1.0					
C37 COMPOUNDS (DIESEL EXHAUST)	30.0			1.0					
C38 COMPOUNDS (DIESEL EXHAUST)	31.0			1.0					
C39 COMPOUNDS (DIESEL EXHAUST)	32.0			1.0					

COMPOUND NAME	PAR	OLE	ETH	TOL	XYL	FORM	ALD2	ISOP	NR
C3/C4/C5 ALKYLBENZENES	3.0			1.0					
C4 ALKYLPHENOLS	3.0			1.0					
C4 ALKYLSTYRENES	3.0	1.0		1.0					
C4 COMPOUNDS (DIESEL EXHAUST)	3.7	0.039					0.111		
C4 OLEFIN	2.0	1.0							
C4 PARAFFIN	4.0								
C4 SUBSTITUTED CYCLOHEXANE	10.0								
C4 SUBSTITUTED CYCLOHEXANONE	10.0								
C40 COMPOUNDS (DIESEL EXHAUST)	33.0			1.0					
C41 COMPOUNDS (DIESEL EXHAUST)	34.0			1.0					
C42 COMPOUNDS (DIESEL EXHAUST)	35.0			1.0					
C43 COMPOUNDS (DIESEL EXHAUST)	36.0			1.0					
C5 ALKYL CYCLOHEXANE	11.0								
C5 ALKYLBENZENES	4.0			1.0					
C5 ALKYLBENZENES (UNSATURATED)	2.0	1.0		1.0					
C5 ALKYLPHENOLS	4.0			1.0					
C5 COMPOUNDS (DIESEL EXHAUST)	4.6	0.045					0.155		
C5 ESTER	6.0								1.0
C5 OLEFIN	3.0	1.0							
C5 PARAFFIN	5.0								
C5 PARAFFIN/OLEFIN	4.0	0.5							
C5 SUBSTITUTED CYCLOHEXANE	11.0								
C5H10O	5.0								
C6 ALKYLBENZENE	5.0			1.0					
C6 COMPOUNDS (DIESEL EXHAUST)	4.5	0.218					0.065		0.934
C6 OLEFINS	4.0	1.0							
C6 PARAFFIN	6.0								
C6 SUBSTITUTED CYCLOHEXANE	12.0								
C6H18O3SI3	6.0								
C7 ALKYLBENZENE	6.0			1.0					
C7 COMPOUNDS (DIESEL EXHAUST)	1.4			0.8					
C7 CYCLOPARAFFINS	7.0								
C7 OLEFINS	5.0	1.0							
C7 PARAFFINS	7.0								
C7H12	5.0	1.0							
C7H12O	5.0	1.0							
C7-C16	11.0								
C8 COMPOUNDS (DIESEL EXHAUST)	4.9	0.21			0.335				
C8 CYCLOPARAFFINS	8.0								
C8 OLEFINS	6.0	1.0							
C8 PARAFFIN	8.0								
C8 PHENOLS	1.0			1.0					
C8H14	6.0	1.0							
C8H24O4SI4	8.0								
C9 COMPOUNDS (DIESEL EXHAUST)	3.62			0.056	0.608		0.062		
C9 CYCLOPARAFFINS	9.0								
C9 OLEFINS	7.0	1.0							
C9 PARAFFIN	9.0								
C9 PHENOLS	2.0			1.0					
CAMPHENE	8.0	1.0							
CAPROLACTAM	5.0								1.0
CARBITOL	2.0						2.0		
CARBON DISULFIDE	1.0								
CARBON TETRACHLORIDE									1.0

COMPOUND NAME	PAR	OLE	ETH	TOL	XYL	FORM	ALD2	ISOP	NR
CARBONYL SULFIDE									1.0
CARYOPHYLLENE	9.0	3.0							
CELLOSOLVE	2.0						1.0		
CELLOSOLVE ACETATE	3.0						1.0		1.0
CHLOROBENZENE	1.0								5.0
CHLORODIFLUOROMETHANE									1.0
CHLOROFORM									1.0
CHLOROPENTAFLUOROETHANE									2.0
CHLOROPRENE		2.0							
CHLOROTRIFLUOROMETHANE									1.0
CHRYSENE				1.0	1.0				3.0
CIS-1,4-DIMETHYLCYCLOHEXANE	8.0								
CIS-2-BUTENE							2.0		
CIS-2-HEPTENE	3.0						2.0		
CIS-2-HEXENE	2.0						2.0		
CIS-2-OCTENE	4.0						2.0		
CIS-2-PENTENE	1.0						2.0		
CIS-3-HEXENE	2.0						2.0		
CORONENE				1.0	1.0				9.0
CREOSOTE	1.0				1.0				2.0
CRESOL				1.0					
CROTONALDEHYDE		1.0					1.0		
CUMENE (ISOPROPYL BENZENE)	2.0			1.0					
CYCLOHEPTANE	7.0								
CYCLOHEXANE	6.0								
CYCLOHEXANOL	6.0								
CYCLOHEXANONE	6.0								
CYCLOHEXENE	2.0						2.0		
CYCLOPENTAANTHRACENES	3.0				1.0				5.0
CYCLOPENTANE	5.0								
CYCLOPENTAPHENANTHRENES	3.0				1.0				5.0
CYCLOPENTA(c,d)PYRENE	2.0			1.0	1.0				1.0
CYCLOPENTENE	1.0						2.0		
CYCLOPENTYLCYCLOPENTANE	10.0								
DECALINS	10.0								
DENATURANT	1.0								
DIACETONE ALCOHOL	4.0						1.0		
DIBENZANTHRACENES	1.0			1.0	1.0				6.0
DIBENZOPYRENES	1.0			1.0	1.0				8.0
DIBENZO(a,h)ANTHRACENE	1.0			1.0	1.0				6.0
DIBENZPHENANTHRENES	1.0			1.0	1.0				6.0
DIBUTYL ETHER	6.0						1.0		
DIBUTYLPHTHALATE	9.0								7.0
DICHLOROBENZENES	1.0								5.0
DICHLORODIFLUOROMETHANE									1.0
DICHLOROMETHANE									1.0
DICHOLROTETRAFLUOROETHANE									2.0
DIETHYLCYCLOHEXANE	10.0								
DIETHYLENE GLYCOL	2.0						1.0		
DIETHYLMETHYLCYCLOHEXANE	11.0								
DIHYDRONAPTHALENE	2.0				1.0				
DIHYDROXYNAPTHALENEDIONE	2.0				1.0				
DIISOPROPYLBENZENE	4.0				1.0				
DIMETHYL ALKYL AMINES	3.0								

COMPOUND NAME	PAR	OLE	ETH	TOL	XYL	FORM	ALD2	ISOP	NR
DIMETHYLBENZYLALCOHOL	1.0				1.0				
DIMETHYLBUTANE	6.0								
DIMETHYLBUTANEDIOATE	4.0								2.0
DIMETHYLBUTENE	4.0	1.0							
DIMETHYLBUTYLCYCLOHEXANE	12.0								
DIMETHYLCYCLOBUTANONE	6.0								
DIMETHYLCYCLOHEXANE	8.0								
DIMETHYLCYCLOPENTANE	7.0								
DIMETHYLCYCLOPENTENES	5.0	1.0							
DIMETHYLDECANE	12.0								
DIMETHYLETHER	2.0								
DIMETHYLETHYLBENZOIC ACID	2.0				1.0				1.0
DIMETHYLETHYLCYCLOHEXANE	10.0								
DIMETHYLFORMAMIDE	2.0								1.0
DIMETHYLHEPTANES	9.0								
DIMETHYLHEPTANOL	9.0								
DIMETHYLHEXADIENE	2.0	1.0					2.0		
DIMETHYLHEXANEDIOATE	6.0								2.0
DIMETHYLHEXANES	8.0								
DIMETHYLHEXENE	6.0	1.0							
DIMETHYLINDANS	3.0				1.0				
DIMETHYLINDENE	1.0	1.0			1.0				
DIMETHYLNAPHTHYRIDINE	3.0			1.0					
DIMETHYLNAPTHALENE	4.0				1.0				
DIMETHYLNONANES	11.0								
DIMETHYLOCTANES	10.0								
DIMETHYLOCTANOL	10.0								
DIMETHYLOCTENES	8.0	1.0							
DIMETHYLOCTYNE	9.0								1.0
DIMETHYLPENTANE	7.0								
DIMETHYLPENTANEDIOATE	5.0								2.0
DIMETHYLPENTANOL	7.0								
DIMETHYLPENTENE	5.0	1.0							
DIMETHYLPHTHALATE	3.0								7.0
DIMETHYLTEREPHTHALATE	3.0								7.0
DIMETHYLUNDECANE	13.0								
DIPHENYLETHANE				2.0					
DIPROPYLENE GLYCOL	4.0						1.0		
DIPROPYLPHTHALATE	7.0								7.0
DIVINYLBENZENE		1.0			1.0				
DI(ETHYLPHENYL)ETHANE	4.0			2.0					
DI-C8 ALKYL PHTHALATE	17.0								7.0
DODECENE	10.0	1.0							
D-LIMONENE	4.0	1.0					2.0		
EICOSANE	20.0								
EPICHLOROHYDRIN	3.0								
ETHANE	0.4								1.6
ETHANOLAMINE	0.4								1.6
ETHYL ACETATE	3.0								1.0
ETHYL ACRYLATE	2.0	1.0							1.0
ETHYL ALCOHOL	0.4								1.6
ETHYL CHLORIDE									2.0
ETHYL ETHER	2.0						1.0		
ETHYLAMINE	0.4								1.6

COMPOUND NAME	PAR	OLE	ETH	TOL	XYL	FORM	ALD2	ISOP	NR
ETHYLBENZENE	1.0			1.0					
ETHYLBICYCLOHEPTANE	16.0								
ETHYLCYCLOHEXANE	8.0								
ETHYLCYCLOPENTANE	7.0								
ETHYLCYCLOPENTENE	5.0	1.0							
ETHYLDIMETHYLBENZENE	2.0				1.0				
ETHYLDIMETHYLCYCLOHEXANE	10.0								
ETHYLDIMETHYLOCTANE	12.0								
ETHYLDIMETHYLPENTANE	9.0								
ETHYLDIMETHYLPHENOL	2.0				1.0				
ETHYLENE			1.0						
ETHYLENE DIBROMIDE									2.0
ETHYLENE DICHLORIDE									2.0
ETHYLENE GLYCOL	0.4								1.6
ETHYLENE OXIDE	1.0								1.0
ETHYLENEAMINES	0.4								1.6
ETHYLFURAN	2.0	2.0							
ETHYLHEPTANE	9.0								
ETHYLHEPTENE	7.0	1.0							
ETHYLHEXANE	8.0								
ETHYLHEXANOATE	7.0								1.0
ETHYLINDAN	3.0				1.0				
ETHYLISOPROPYL ETHER	3.0						1.0		
ETHYLMERCAPTAN	2.0								
ETHYLMETHYLCYCLOHEXANE	9.0								
ETHYLMETHYLCYCLOPENTANE	8.0								
ETHYLMETHYLHEXANE	9.0								
ETHYLMETHYLOCTANE	11.0								
ETHYLOCTANE	10.0								
ETHYLOCTENE	8.0	1.0							
ETHYLPENTENE	5.0	1.0							
ETHYLPHENYLPHENYLETHANE	1.0			1.0	1.0				
ETHYLPROPYLCYCLOHEXANE	11.0								
ETHYLSTYRENE	1.0	1.0		1.0					
ETHYLTOLUENE	1.0				1.0				
ETHYL-T-BUTYL ETHER	4.0						1.0		
FLUORANTHENE				1.0	1.0				1.0
FLUORENE					1.0				5.0
FORMALDEHYDE						1.0			
FORMIC ACID									1.0
FURFURYL ALCOHOL	1.0	2.0							
GLYCEROL	1.5								1.5
GLYCOL	0.4								1.6
GLYCOL ETHER	0.8								3.2
GLYOXAL	1.0					1.0			
HENEICOSANE	21.0								
HEPTADIENAL	1.0	1.0					2.0		
HEPTANE	7.0								
HEPTANONE	7.0								
HEPTENE	5.0	1.0							
HEXADECANE	16.0								
HEXADECANOIC ACID	15.0								1.0
HEXADIENAL		1.0					2.0		
HEXAFLUOROETHANE									2.0

COMPOUND NAME	PAR	OLE	ETH	TOL	XYL	FORM	ALD2	ISOP	NR
HEXAMETHYLENEDIAMINE	6.0								
HEXANAL	4.0						1.0		
HEXANE	6.0								
HEXENE	4.0	1.0							
HEXYLENE GLYCOL	6.0								
HEXYNE	5.0								1.0
INDANE	1.0				1.0				
INDENE		0.5			1.0				
INDENO(1,2,3-cd)PYRENE		1.0		1.0	1.0				4.0
ISOAMYL ALCOHOL	5.0								
ISOAMYLBENZENE	4.0			1.0					
ISOBUTANE	4.0								
ISOBUTYL ALCOHOL	4.0								
ISOBUTYLACETATE	5.0								1.0
ISOBUTYLACRYLATE	4.0	1.0							1.0
ISOBUTYLBENZENE	3.0			1.0					
ISOBUTYLENE	2.0	1.0							
ISOBUTYLISOBUTYRATE	7.0								1.0
ISOBUTYRALDEHYDE	2.0						1.0		
ISOMERS OF BUTENE	2.0	1.0							
ISOMERS OF BUTYLBENZENE	3.0			1.0					
ISOMERS OF C10H10		1.0			1.0				
ISOMERS OF C10H18	8.0	1.0							
ISOMERS OF C11H20	11.0								
ISOMERS OF C9H16	7.0	1.0							
ISOMERS OF DECANE	10.0								
ISOMERS OF DIETHYLBENZENE	2.0				1.0				
ISOMERS OF DODECANE	12.0								
ISOMERS OF ETHYLTOLUENE	1.0				1.0				
ISOMERS OF HEPTADECANE	17.0								
ISOMERS OF HEPTANE	7.0								
ISOMERS OF HEXANE	6.0								
ISOMERS OF NONANE	9.0								
ISOMERS OF OCTADECANE	18.0								
ISOMERS OF OCTANE	8.0								
ISOMERS OF PENTADECANE	15.0								
ISOMERS OF PENTANE	5.0								
ISOMERS OF PENTENE	3.0	1.0							
ISOMERS OF PROPYLBENZENE	2.0			1.0					
ISOMERS OF TETRADECANE	14.0								
ISOMERS OF TRIDECANE	13.0								
ISOMERS OF UNDECANE	11.0								
ISOMERS OF XYLENE					1.0				
ISOOCTANE	8.0								
ISOPENTANE	5.0								
ISOPRENE								1.0	
ISOPROPYL ALCOHOL	1.5								1.5
ISOPROPYLACETATE	4.0								1.0
ISOPROPYLBENZENE	2.0			1.0					
ISOPROPYLCYCLOHEXANE	9.0								
ISOPROPYLCYCLOPENTANE	8.0								
ISOPROPYLMETHYLCYCLOHEXANE	10.0								
ISOVALERALDEHYDE	3.0						1.0		
LACTOL SPIRITS	8.0								

COMPOUND NAME	PAR	OLE	ETH	TOL	XYL	FORM	ALD2	ISOP	NR
LIMONENE	4.0	1.0					2.0		
MALEIC ANHYDRIDE		2.0							
METHANE									
METHOXYETHOXYBUTANONE	5.0						1.0		
METHOXYETHOXYETHANOL	3.0						1.0		
METHOXYNAPHTHALENE	3.0				1.0				
METHYL ALCOHOL	1.0								
METHYL C11 ESTER	12.0								1.0
METHYL C12 ESTER	13.0								1.0
METHYL C13 ESTER	14.0								1.0
METHYL C14 ESTER	15.0								1.0
METHYL C15 ESTER	16.0								1.0
METHYL C19 ESTER	20.0								1.0
METHYL C20-ESTER	21.0								1.0
METHYLACETATE	2.0								1.0
METHYLACETOPHENONE	1.0			1.0					1.0
METHYLACETYLENE (PROPYNE)	2.0								1.0
METHYLACRYLATE	1.0	1.0							1.0
METHYLAL	3.0								
METHYLALLENE	1.0	1.5							
METHYLAMYL KETONE	7.0								
METHYLANTHRACENES	2.0				1.0				5.0
METHYLBENZANTHRACENES	1.0			1.0	1.0				3.0
METHYLBENZPHENANTHRENE	1.0			1.0	1.0				3.0
METHYLBIPHENYL					1.0				5.0
METHYLBUTADIENE	1.0	2.0							
METHYLBUTENE	3.0	1.0							
METHYLBUTYL KETONE	6.0								
METHYLCARBITOL	3.0						1.0		
METHYLCELLOSOLVE	1.0						1.0		
METHYLCHLORIDE									1.0
METHYLCHRYSENES	1.0			1.0	1.0				3.0
METHYLCYCLOHEXADIENE	1.0	1.0					2.0		
METHYLCYCLOHEXANE	7.0								
METHYLCYCLOHEXENE	5.0	1.0							
METHYLCYCLOOCTANE	9.0								
METHYLCYCLOPENTADIENE		1.0					2.0		
METHYLCYCLOPENTANE	6.0								
METHYLCYCLOPENTENE	4.0	1.0							
METHYLDECALINS	11.0								
METHYLDECANES	11.0								
METHYLDECENE	9.0	1.0							
METHYLDIHYDRONAPHTHALE	3.0				1.0				
METHYLDODECANE	13.0								
METHYLDODECANOATE	12.0								1.0
METHYLENE BROMIDE									1.0
METHYLENE CHLORIDE									1.0
METHYLENEBIS(C6H4NCO)	1.0			1.0					7.0
METHYLENE(b)4-PHENYLISOCYANATE				1.0					8.0
METHYLETHYL KETONE	4.0								
METHYLETHYLHEPTANE	10.0								
METHYLETHYLPENTANOATE	7.0								1.0
METHYLFLUORANTHENES	1.0			1.0	1.0				1.0
METHYLFORMATE	1.0								1.0

COMPOUND NAME	PAR	OLE	ETH	TOL	XYL	FORM	ALD2	ISOP	NR
METHYLGLYOXAL						1.0	1.0		
METHYLHEPTANE	8.0								
METHYLHEPTANOL	8.0								
METHYLHEPTENE	6.0	1.0							
METHYLHEPTYNE	7.0								1.0
METHYLHEXADIENE	1.0	1.0					2.0		
METHYLHEXANAL	5.0						1.0		
METHYLHEXANE	7.0								
METHYLHEXENES	5.0	1.0							
METHYLINDANS	2.0				1.0				
METHYLINDENE		1.0			1.0				
METHYLISOBUTYL KETONE	6.0								
METHYLISOPROPYLCYCLOHEXANE	10.0								
METHYLMETHACRYLATE	2.0	1.0							1.0
METHYLMETHYLPROPENOATE	2.0	1.0							1.0
METHYLMYRISTATE	14.0								1.0
METHYLNAPHTHALENES	3.0				1.0				
METHYLNONANE	10.0								
METHYLNONENE	8.0	1.0							
METHYLOCTANES	9.0								
METHYLPALMITATE	16.0								1.0
METHYLPENTANE	6.0								
METHYLPENTENES	4.0	1.0							
METHYLPHENANTHRENES	2.0				1.0				5.0
METHYLPROPYLCYCLOHEXANE	10.0								
METHYLPROPTLNONANE	13.0								
METHYLSTEARATE	18.0								1.0
METHYLSTYRENE		1.0		1.0					
METHYLUNDECANE	12.0								
METHYL-T-BUTYL ETHER	3.0						1.0		
MINERAL SPIRITS	6.0						1.0		
MYRCENE	4.0	3.0							
M-DICHLOROBENZENE	1.0								5.0
M-DIETHYLBENZENE	2.0				1.0				
M-ETHYLTOLUENE	1.0				1.0				
M-XYLENE					1.0				
M-XYLENE AND P-XYLENE					1.0				
NAPHTHA	8.0								
NAPTHALENE	2.0				1.0				
NITROBENZENE	1.0								5.0
NONADECANE	19.0								
NONADIENE	3.0	1.0					2.0		
NONANE	9.0								
NONENE	7.0	1.0							
NONENONE	7.0	1.0							
NONYLPHENOL	8.0			1.0					
N-AMYLBENZENE	4.0			1.0					
N-BUTANE	4.0								
N-BUTYL ALCOHOL	4.0								
N-BUTYLACETATE	5.0								1.0
N-DECANE	10.0								
N-DODECANE	12.0								
N-HEPTADECANE	17.0								
N-HEXYLBENZENE	5.0			1.0					

COMPOUND NAME	PAR	OLE	ETH	TOL	XYL	FORM	ALD2	ISOP	NR
N-PENTADECANE	15.0								
N-PENTANE	5.0								
N-PENTENE	3.0	1.0							
N-PENTYLCYCLOHEXANE	11.0								
N-PHENYLANILINE				1.0					5.0
N-PROPYL ALCOHOL	1.5								1.5
N-PROPYLACETATE	4.0								1.0
N-PROPYLBENZENE	2.0			1.0					
N-TETRADECANE	14.0								
N-TRIDECANE	13.0								
N-UNDECANE	11.0								
OCTAHYDROINDENES	9.0								
OCTAMETHYLCYCLOTETRASILOXANE	8.0								
OCTANE	8.0								
OCTANOL	8.0								
OCTATRIENE		2.0					2.0		
OCTENE	6.0	1.0							
OXYGENATES	4.0								
O-DICHLOROBENZENE	1.0								5.0
O-ETHYLTOLUENE	1.0				1.0				
O-XYLENE					1.0				
PALMITIC ACID	15.0								1.0
PARAFFINS (C16-C34)	25.0								
PARAFFINS (C2-C7)	4.5								
PARAFFINS/OLEFINS (C12-C16)	13.0	0.5							
PENTADIENE	1.0	2.0							
PENTANOL	5.0								
PENTENYNE	2.0	1.0							1.0
PENTYLBENZENE	4.0			1.0					
PENTYLCYCLOHEXANE	11.0								
PENTYLIDENECYCLOHEXANE	10.0	1.0			0.0				
PENTYNE	4.0								1.0
PERCHLOROETHYLENE									2.0
PERYLENE				1.0	1.0				5.0
PHENANTHRENE	1.0				1.0				5.0
PHENOL	1.0								5.0
PHENYLISOCYANATE	1.0								6.0
PHENYLNAPHTHALENES	1.0			1.0	1.0				
PHTHALIC ANHYDRIDE	1.0								7.0
PIPERYLENE	1.0	2.0							
POLYETHYLENE GLYCOL	2.0								
PROPADIENE		1.5							
PROPANE	1.5								1.5
PROPENE	1.0	1.0							
PROPENYLCYCLOHEXANE	7.0	1.0							
PROPIONALDEHYDE	1.0						1.0		
PROPIONIC ACID	2.0								1.0
PROPYLBENZENE	2.0			1.0					
PROPYLCYCLOHEXANE	9.0								
PROPYLENE DICHLORIDE	1.5								1.5
PROPYLENE GLYCOL	1.5								1.5
PROPYLENE OXIDE	2.0								1.0
PROPYLHEPTENES	8.0	1.0							
PYRENE				1.0	1.0				1.0

COMPOUND NAME	PAR	OLE	ETH	TOL	XYL	FORM	ALD2	ISOP	NR
P-DICHLOROBENZENE	1.0								5.0
P-ETHYLTOLUENE	1.0				1.0				
P-TOLUALDEHYDE							2.0		4.0
P-XYLENE					1.0				
SEC-BUTYL ALCOHOL	4.0								
SEC-BUTYLBENZENE	3.0			1.0					
SILOXANE									
STYRENE		0.5		1.0					
SUBSTITUTED C9 ESTER (C12)	12.0								1.0
TEREPHTHALIC ACID	1.0								7.0
TERPENES	8.0	1.0							
TETRACHLOROBENZENES	1.0								5.0
TETRAFLUOROMETHANE									1.0
TETRAMETHYLBENZENE	2.0				1.0				
TETRAMETHYLCYCLOBUTENE	6.0	1.0							
TETRAMETHYLCYCLOPENTANE	9.0								
TETRAMETHYLHEXANE	10.0								
TETRAMETHYLPENTANONE	9.0								
TETRAMETHYLSILANE	4.0								
TETRAMETHYLTHIOUREA	4.0								1.0
TOLUENE				1.0					
TOLUENE DIISOCYANATE				1.0					2.0
TOLUENE ISOCYANATE				1.0					1.0
TOTAL AROMATIC AMINES	1.0								5.0
TOTAL C2-C5 ALDEHYDES	1.5						1.0		
TRANS-1-PHENYLBUTENE	1.0	1.0		1.0					
TRANS-2-BUTENE							2.0		
TRANS-2-HEPTENE	3.0						2.0		
TRANS-2-HEXENE	2.0						2.0		
TRANS-2-NONENE	5.0						2.0		
TRANS-2-PENTENE	1.0						2.0		
TRANS-3-HEXENE	2.0						2.0		
TRICHLOROBENZENES	1.0								5.0
TRICHLOROFLUOROMETHANE									1.0
TRICHLOROTRIFLUOROETHANE									2.0
TRICHOLROETHYLENE			1.0						
TRIETHYLENE GLYCOL	2.0						2.0		
TRIFLUOROMETHANE									1.0
TRIMETHYLAMINE	3.0								
TRIMETHYLBENZENE	1.0				1.0				
TRIMETHYLCYCLOHEXANES	9.0								
TRIMETHYLCYCLOHEXANOL	9.0								
TRIMETHYLCYCLOPENTANE	8.0								
TRIMETHYLCYCLOPENTANONE	8.0								
TRIMETHYLDECANE	13.0								
TRIMETHYLDECENE	11.0	1.0							
TRIMETHYLFLUOROSILANE	2.0								1.0
TRIMETHYLHEPTANES	10.0								
TRIMETHYLHEXANES	9.0								
TRIMETHYLHEXENE	7.0	1.0							
TRIMETHYLINDAN	4.0				1.0				
TRIMETHYLNONENE	10.0	1.0							
TRIMETHYLOCTANES	11.0								
TRIMETHYLPENTADIENE	4.0	2.0							

COMPOUND NAME	PAR	OLE	ETH	TOL	XYL	FORM	ALD2	ISOP	NR
TRIMETHYLPENTANE	8.0								
T-BUTYL ALCOHOL	4.0								
T-BUTYLBENZENE	2.0			1.0					1.0
UNIDENTIFIED	6.0								
VINYL ACETATE	1.0	1.0							1.0
VINYL CHLORIDE			1.0						
XYLENE BASE ACIDS					1.0				

TABLE C-2. EXAMPLE PROBLEM* - PART I

COMPUTATION OF CARBON BOND CONCENTRATIONS

Measured Compound   Carbon Bond Concentration

Species	ppbC	ppb	OLE	PAR	TOL	XYL	FORM	ALD2	ETH	NR	ISOP
Ethylene	20	10							10		
Propene	30	10	10	10							
n-Butane	170	42.5		170							
T-2-Butane	10	2.5						5			
2,3-Dimethylbutane	100	16.7		100							
Toluene	70	10			10						
M-xylene	40	5				5					
Benzene	60	10		10						50	
TOTAL	500	106.7	10	290	10	5	0	5	10	50	0

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*This is a hypothetical problem, and is not necessarily intended to be indicative of the NMOC composition of ambient air.

TABLE C-3. EXAMPLE PROBLEM - PART 2

COMPUTATION OF CARBON-FRACTIONS

B-4 Class	Concentration (ppb)[1]	Concentration (ppbC)[2]	Initial Carbon Fraction[3]	Final Carbo Fraction[4]
OLE	10	20	0.04	0.04
PAR	290	290	0.58	0.55
TOL	10	70	0.14	0.13
XYL	5	40	0.08	0.08
FORM	0	0	0.00	0.02
ALD2	5	10	0.02	0.05
ETH	10	20	0.04	0.04
ISOP	0	0	0.00	0.00
NR	50	50	0.10	0.09
OTAL		500	1.00	1.00

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[1] From Table C-2

[2] Computed by taking concentration in ppb times carbon numbers from Table 2-1.

[3] Computed by dividing concentrations in ppbC by the total NMOC in ppbC (e.e., 500 ppbC).

[4] Unmeasured aldehydes added (.02 to FORM AND .03 to ALD2) and total readjusted to 1.00.

The individual concentrations in the nine entries in the right hand column are obtained by multiplying the concentration of each species times the number of bonds for that species found in Table C-1. For example, propene has a concentration of 10 ppb in the example problem. Table C-1 shows that propene has one olefin bond and one paraffin bond. Thus, 10 ppb are put in each category (OLE and PAR).

After all of the species concentrations have been apportioned to the carbon bond groups, then each column is totalled. These concentrations are in ppb. To convert to ppbC, the assumed carbon number for each carbon bond class are utilized. These are found in Table 2-1. When the concentrations in ppb are multiplied by these carbon numbers, concentrations in ppbC are obtained.

Each total for a carbon bond class is then divided by the total NMOC (in ppbC) to obtain initial carbon-fractions. The final step is to add 0.02 to the FORM fraction and 0.03 to the ALD2 fraction. These adjustments are to account for aldehydes which are not detected by the sampling/analytical procedure. The fractions are then adjusted so that they total up to 100 percent.

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Procedures for Applying City-Specific EKMA		5. REPORT DATE
		6. PERFORMING ORGANIZATION CODE
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15. SUPPLEMENTARY NOTES

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16. ABSTRACT

OZIPM-4 is a model which allows the user to estimate the volatile organic compound (VOC) control requirement for a city in order to achieve the national ambient air quality standard for ozone.

This manual outlines the inputs required to run OZIPM-4 and explains how to develop the needed variables.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
ozone VOC control strategies photochemical modeling		

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